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**PART VI**

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**PROCEEDINGS**  
**OF**  
**THE SYMPOSIUM**  
**ON**  
**ROLE OF PHOSPHATES IN THE SOIL,**  
**PLANT AND ANIMAL KINGDOM**  
**PART III**

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**ALLAHABAD**

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Vol. XXV

SECTION-A

Part VI

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**MECHANISM OF PHOSPHATE LEACHING FROM SOILS**

By

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The low phosphate status of many soils of the world has drawn the attention of soil scientists for a long time and as phosphate is indispensable for proper crop growth, a systematic and comprehensive investigation on the loss of phosphates from various soils under different climatic conditions has been undertaken in this laboratory. Russell<sup>1</sup> while summarizing the importance of phosphates in soils has observed as follows :—

“Most soils contain insufficient phosphate to satisfy the large crops produced by the modern farmers, frequent additions are therefore necessary. The losses are not as serious as those of nitrogen. There is practically no washing out, the agricultural chemist can still detect the phosphates added to the lands round the cities of ancient Egypt. Nevertheless there is a continuous and steady loss in the crops which has to be made good. There is no way of adding a single ounce of world stock of phosphorus compounds and this is being drawn upon even now to the extent of some million tons each year while the demand increases steadily as time goes on. If some day the supply gives out and at present it seems inevitable that it must, mankind will be faced with perhaps the most serious of all catastrophes, a phosphorus famine. .... we must therefore look to the ocean for the means of replacing the land deposits of phosphates.”

In many American publications<sup>2</sup>, the analyses of well-waters, drainage waters and irrigation waters, 0.2% salt content has been observed but the amount of phos-

phate has been found to be negligible. Similarly most soil solutions from alkaline and saline soils lack in phosphate contents.

Bingham<sup>3</sup> working with Californian soils and using a soil water ratio of 1 : 10 concluded that where the filtrate contained less than 0.4 p. p. m. of phosphate, the soils responded to phosphatic fertilizers. Burd and Martin<sup>4</sup> and Pierre and Parker<sup>5</sup> have shown that the concentrations of P in water are of the same order and much less than 1 p. p. m. In some productive soils studied, Parker and Tidmore<sup>6</sup> have found that water-extracts and displaced soil-solutions were more dilute in P than the minimum concentration necessary for good plant growth in nutrient solutions. Teakle<sup>7</sup> obtained the concentration of displaced phosphate to be extremely low from soils of known acceptable productivity, however it is seldom below 0.05 p. p. m. and rarely above 10 p. p. m. In conventional nutrient solutions, the concentration of phosphoric acid is of the order of 100 or more p. p. m. and the concentration in the plant sap is usually hundered to several hundreds p. p. m. as reported by Tidmore<sup>8</sup>, Pierre and Pohlman<sup>9</sup>. In the earliest experiments Ulbricht, Schloesing, Whitney, Kind and Schultze<sup>10</sup> obtained variable results by displacement techniques, the amounts of  $P_2O_5$  in soil solutions ranged from 1 p. p. m. to 16.96 p. p. m. in poor and good soils.

Way<sup>11</sup> was the first to analyse drainage waters from many plots in which he obtained only small amounts of phosphates. Voelcker<sup>12</sup> found that the drainage water from Broadbalk fields at Rothamsted gave 0.6 and 1.54 p. p. m. of  $P_2O_5$  in unmanured and manured plots respectively. Hall<sup>13</sup> pointed out that the Rothamsted surface soils lose 1 Kgm. of  $P_2O_5$  per acre by leaching. Burd and Martin<sup>14</sup> have examined the soil solutions of certain Californian soils using a method of displacement under pressure and have found 0.6 to 1.1 p. p. m. of  $PO_4'''$ . Lyon and Buckman<sup>15</sup> have summarized the amounts of elements lost in drainage water in which 3–7 lbs. of N, 4 lbs.  $P_2O_5$ , 75 lbs.  $K_2O$ , 40 lbs. S, 350 lbs. CaO and 80 lbs. MgO were lost per acre. MacIntire and Sterges<sup>16</sup> have reported a loss of 0.3 lbs. of P from a soil having a pH between 6.7–7.4 and receiving 50.8 inches rain annually. By the application of 2 tons of  $CaCO_3$  in the form of limestone or basic slag, the amount of phosphate washed away decreased in presence of  $CaCO_3$  but increased when basic slag was added.

Marked losses of phosphates from soils by washings have been reported by Robinson and Jones<sup>17</sup> from the wet soils of Wales where the rainfall is high. Iversen<sup>18</sup> has reported a loss of phosphates from average mineral and organic soils of Denmark in areas of average rainfall varying from 0.4 to 3.6 Kgm. of  $P_2O_5$  per hectare. Beater<sup>19</sup>, Roger<sup>20</sup>, Kardos<sup>21</sup> and Scarseth and Chandler<sup>22</sup> have reported that loss of phosphate may be serious where there is much run-off water. Some workers like Doak<sup>23</sup>, MacIntire and coworkers<sup>24</sup> and Neller<sup>25</sup> have reported losses from sandy soils. Jacobson, Swanson and Smith<sup>26</sup> have reported losses from soils receiving unusually heavy phosphate applications. Glentworth<sup>27</sup> suggests that there might be a loss of P in ground water of poorly drained soils. Gruness, Hass and Shih<sup>28</sup> have reported the amounts of water soluble  $P_2O_5$  in pounds per acre from the manured cereal plots, unmanured rotational plots, manured rotational plots and virgin plots to be 8.77, 4.39, 44.9 and 4.4 respectively.

The organic matter content of soils and the fertilization practices also affect the loss of phosphates from the soils to a great deal. Gaarder<sup>29</sup> stated that in humid or semi-humid soils of high humus content, the loss of phosphate may be very great. Russell<sup>30</sup> has reported 4.463 p. p. m., of  $P_2O_5$  from the plots which received farmyard manure whilst to which phosphatic fertilizers were added lost



4.39 p. p. m. in comparison to the plot without any treatment which lost only 0.525 p. p. m. of  $P_2O_5$ . Jensen<sup>31</sup> concluded that the water-extracts of decomposing organic material were much more effective than water in dissolving phosphates from the soils. Gaarder and Grahl Nielson<sup>32</sup> found lower amounts of water soluble phosphates in soils poorly supplied than in soils well supplied with organic matter. McGeorge<sup>33</sup> also found that after 3 years of application of superphosphate to a soil whose loss on ignition was 10%, reverted to its original P-level.

A number of workers have reported greater losses of phosphates by the presence of salts whilst others obtained contrary results. According to Liebig<sup>34</sup> NaCl,  $NaNO_3$  and ammonium salts increase the water solubility of calcium phosphates. Dyer<sup>35</sup> found that salts of sodium, potassium and ammonium facilitated the penetration of phosphate to greater depths. McGeorge and Breazeale<sup>36</sup> observed that neutral salts decreased the solubility of rock phosphate and soil phosphates. Greaves<sup>37</sup> found that NaCl, KCl,  $CaCl_2$ ,  $NaNO_3$  and  $CaSO_4$  decreased their solubility and  $NaNO_3$ ,  $K_2SO_4$  and  $(NH_4)_2SO_4$  increased it, while Midgley<sup>38</sup> obtained contrary results. On the other hand, Brown<sup>39</sup> showed that  $NaNO_3$  and  $(NH_4)_2SO_4$  did not increase phosphate in the extracts. Hibbard<sup>40</sup> reported that  $CaSO_4$  and  $CaCO_3$  depressed the solubility of soil phosphates whilst  $Na_2SO_4$  and  $(NH_4)_2SO_4$  had no effect. Eriksson<sup>41</sup> using Swedish soils found that the solubility of soil phosphate was lowered by KCl. Similar results were obtained by Kurtz<sup>42</sup> et al. Cameron and Hurst<sup>43</sup> found that neutral salts depressed the solubility of  $AlPO_4$ . Similar observations were made by Mattson and Karlsson<sup>44</sup>. Teakle<sup>45</sup> rendered the calcium of soil inactive by pretreatment with ammonium oxalate and then found a marked increase in phosphate solubility. Lehr and Van weselmael<sup>46</sup> found that  $NaNO_3$ ,  $Ca(NO_3)_2$  and  $Na_2SO_4$  decreased the solubility of soil phosphates while  $KNO_3$  increased it. In recent papers Dhar<sup>47</sup> and Dhar and Misra<sup>48</sup> have reported beneficial effect of adding phosphates in decreasing loss of lime from the soils.

As no data regarding the losses of phosphates from Indian soils are available, the present investigations were undertaken to find out the relative losses of phosphates from two soils of Allahabad when they are leached repeatedly with distilled water or salt solutions in the laboratory. One of the soils is poor in organic matter, lime and phosphate status while the other is rich in them.

#### EXPERIMENTAL PROCEDURE

Two soils, whose analyses are given in table 1, were passed through 100 mesh-sieve. Known weights of air-dry samples were shaken with different amounts of distilled water in glass stoppered bottles for two hours and then filtered through a Buchner funnel under pressure after 48 hours. The soils were again transferred to the bottles with distilled water, the volume was made up and shaken as before. In this way from 18 to 50 washings were taken with soil-water ratios of 1 : 2, 1 : 3, 1 : 5, 1 : 10, 1 : 25, 1 : 50 and 1 : 100 to imitate the leachings of soils in nature under different rainfalls. The soils were then analysed for their residual  $P_2O_5$  contents and the deficit in  $P_2O_5$  from the initial contents gave the amounts of  $P_2O_5$  lost in all washings. These losses were calculated in pounds per acre, assuming the weight of one acre of soil upto 9 inches to be 1000 tons. The various extracts from washings were also analysed for their  $P_2O_5$  contents but as the amounts in many extracts could not be determined by the phosphoammonium molybdate precipitation method, the total amount of  $P_2O_5$  lost was found out from the difference in  $P_2O_5$  before and after leaching the soils with distilled water.

The soils were also shaken and washed repeatedly with 0.01M, NaCl and KCl solutions. In order to find out a possible mechanism of the loss of phosphates from soils by leaching, the hydrolysis of  $\text{FePO}_4$ ,  $\text{AlPO}_4$ ,  $\text{CaHPO}_4$  and  $\text{Ca}_3(\text{PO}_4)_2$  was investigated at 25°C. The effect of adding  $\text{CaCO}_3$ , basic slag or rock phosphate to the system was also studied. In some experiments carbon dioxide was also passed in the suspensions of basic slag, rock phosphate,  $\text{CaHPO}_4$  and  $\text{Ca}_3(\text{PO}_4)_2$  in distilled water.

## RESULTS

TABLE No. 1

*Composition of soils used in experiments. (Per cent)*

Soils	Carbon	Sesqui-oxides	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	P <sub>2</sub> O <sub>5</sub>	pH
Good soil	... 1.44	9.83	4.35	4.08	1.77	0.418	7.6
Normal soil	... 0.44	11.17	4.12	1.00	1.16	0.079	7.6

TABLE No. 2

*Loss of  $\text{P}_2\text{O}_5$  from soils at different soil-water ratios in lbs./acre.*

	Soil-water ratios.						
	1:2	1:3	1:5	1:10	1:25	1:50	1:100
<b>Good Soil</b>							
Total loss of $\text{P}_2\text{O}_5$ in lbs./acre ...	112.0	134.9	136.9	403.2	1504.8	2598.4	4659.2
Loss per washing (lbs./acre) ...	6.2	7.5	7.6	8.0	30.0	51.96	93.2
<b>Normal Soil</b>							
Total loss of $\text{P}_2\text{O}_5$ in lbs./acre ...	11.2	...	...	22.8	33.6	...	...
Loss per washing (lbs./acre) ...	0.25	...	...	0.57	0.75	...	...

TABLE No. 3

*Loss of  $\text{P}_2\text{O}_5$  in different washings of good soil in lbs./acre.*

Washings	...	Soil-water ratios		
		1:10	1:25	1:50
First	...	107.5	224.0	246.0
Seventh	...	92.5	192.4	212.8
Tenth	...	25.0	79.7	103.0
Seventeenth	...	24.5	78.4	85.1

TABLE No. 4

Solubility of soil phosphate in salt solutions of 0.01M conc.

Loss of  $P_2O_5$  in lbs./acre per washing at 1:2 soil-solution ratio.

Soils	0.01M NaCl	0.01M $Na_2SO_4$	0.01M $K_2SO_4$	0.01M KCl
Good soil	13.6	14.0	13.21	12.61
Normal soil	5.4	5.6	4.8	4.5

## DISCUSSION

From a close study of the foregoing results, it is clear that a phosphate-rich good soil loses more phosphate per washing than the phosphate-poor soil and the amount of phosphate lost from the good soil at higher soil-water ratios is much greater than from most of the soils of the world. Even after the seventeenth washing the good quality soil loses appreciable amounts of phosphate, hence it is clear that such phosphate-rich soils can lose phosphate steadily where rainfall is high, whilst a phosphate-poor soil is resistant to such leaching by rains.

From table No. 2, it can be calculated that assuming the average rainfall at a station to be 25 inches per year, about 112 lbs. of  $P_2O_5$  are lost in 18 years (soil-water ratio 1:2), 135 lbs. of  $P_2O_5$  in 36 years (1:5 ratio), 400 lbs. in 200 years (1:10 ratio), 1500 lbs. in 500 years (1:25 ratio), 2600 lbs. in 1000 years (1:50 ratio) and 4660 lbs. in about 2000 years from the good quality soil while from the normal soil, poor in phosphate, 11.2 lbs. of  $P_2O_5$  can be lost in 50 years (1:2 ratio) and 33.6 lbs. in 5000 years (1:25 ratio). Calculating these amounts as the percentage of total  $P_2O_5$ , they seem to vary from 1.2% to 5.2% in the case of good soil while 0.63% to 1.9% in the case of normal soil. Hence it is clear that from the good quality soil about half of the total  $P_2O_5$  can be lost in 2000 years whilst it will take about 12500 years for the normal soil to wash half of its total  $P_2O_5$ . Leeper<sup>49</sup> working with Australian soils has calculated that at Melbourne where the rainfall is 20 inches per year and the amount of P per acre in drainage water is 2 lbs., it will require 15000 years to wash off half of P from 2 tons of  $P_2O_5$  per acre of the soil. Mattson<sup>50</sup> has found that taking the solubility of P under field conditions as in water systems, the weight of the cultivated layer to be 3 Kgm. per  $dm^2$ , the adsorbed  $P_2O_5$  of the soil to be 930 mgm. per  $dm^2$ , and a leaching of one litre per  $dm^2$  representing 10 cm. of rainfall would remove 0.62 mgm. of  $P_2O_5$  i. e. 0.066% of adsorbed P whilst the loss will be 0.0071 mgm. i. e. 0.003% from a soil where the adsorbed P is 242 mgm. per  $dm^2$ . Thus he concludes that at lower levels of phosphate status, the loss resulting from a moderate leaching becomes very small and the depletion of adsorbed phosphate would be even slower than indicated by leaching. These results support our view that a phosphate poor soil loses less phosphate on leaching. In other words, the soil solution contains less phosphate ions, hence the crops can obtain very little of phosphate in the soluble form. On the other hand, the good soil, being rich in organic matter and phosphate can be a very good source of soluble phosphates for a growing crop. However, under ordinary natural conditions such drastic leachings or washings of the soils can not take place because the time of contact of the percolating waters with the soil particles is not very long and hence the loss of phosphate in drainage is meagre.

The effect of soil-water ratio on the amount of  $P_2O_5$  in the successive filtrates is very interesting. As the amount of water is increased, more of  $P_2O_5$  comes into solution which shows that the phosphate in solution is being made available by the hydrolysis of various phosphates present in the soil. According to McGeorge and Fuller<sup>51</sup> in the repeated extraction of phosphates at 1:5 soil-water ratio from many calcareous soils of Arizona, appreciable amounts of phosphate are available even after 7 or 8 extractions. By varying the soil-water ratio from 1:2 to 1:10, they obtained greater amounts of phosphate in solution. Their results are :—

Amount of  $P_2O_5$  in p. p. m.

No. of extracts	...	1	2	3	4	5	6	7	8	9
Inorganic phosphate		7.6	7.5	6.1	5.0	3.0	2.3	1.9	1.7	1.4
pH	...	8.5	8.5	8.65	8.6	8.6	8.5	8.4	8.4	...

Fuller and McGeorge<sup>52</sup> have found that the organic and inorganic phosphates in black alkali soil or in high sodium-soil is notably greater, hence they concluded that other cations besides calcium exert some influence on phosphate solubility. It seems that in water-extracts the presence of calcium ions decrease the phosphate solubility by the common ion effect but in the presence of Na or K ions, which have no common ions with the calcium phosphates, the activity coefficients of calcium and phosphate ions decrease. This means that the solubility of calcium phosphate should increase. This phenomenon has been termed by Lewis and Randall as the "Salt effect". A similar view has been supported by Wild<sup>53</sup>.

For a long time  $Ca_3(PO_4)_2$ ,  $FePO_4$  and  $AlPO_4$  have been considered to be present in the soils. It has also been reported that these phosphates being sparingly soluble dissociate in negligible amounts to furnish little phosphate ions in the water extracts. However, Cameron and Bell<sup>54</sup> for the first time showed that  $Ca_3(PO_4)_2$ ,  $FePO_4$  and  $AlPO_4$  undergo hydrolysis to produce a more alkaline phosphate. In this way they concluded that in acidic soils where iron and aluminium phosphates predominate, their leaching may lead to an impoverishment of phosphate ions with a result to form more basic phosphates of iron and aluminium which are less soluble. We have found that  $Ca_3(PO_4)_2$ ,  $FePO_4$  and  $AlPO_4$  hydrolyse to a great extent but  $CaHPO_4$  undergoes very little hydrolysis and dissolves usually as such or more calcium is given out than the theoretical value. The following results were obtained by shaking 1.25 gms. of the various phosphates with 150 c. c. distilled water for two hours and filtering after 24 hours' contact. More than 4 such successive washings were carried on.

No. of washings	Amount of $P_2O_5$ in grams from the phosphates			$CaHPO_4$
	$AlPO_4$	$FePO_4$	$Ca_3(PO_4)_2$	
1	0.00780	0.00195	0.01980	0.00525
2	0.00535	0.00103	0.01087	0.00364
3	0.00506	0.00075	0.01032	0.00364
4	0.00560	0.00075	0.00914	0.00340
5	0.00548	0.00073	0.00748	0.00332

The extent of hydrolysis can also be judged from the relative amounts of calcium and phosphate in the extracts of the calcium phosphates. When these are dissolved without any hydrolysis, in the extracts the ratio  $\text{CaO} : \text{P}_2\text{O}_5$  should be 3:1 or 2:1 with tricalcium and dicalcium phosphates respectively. But from the results recorded below it is seen that this ratio frequently reaches the value 2.3:1 in tricalcium phosphate while it is 2:1 for dicalcium phosphate in the beginning but later on it reaches even more than 3:1. The results show marked hydrolysis in the case of tricalcium phosphate forming monocalcium phosphate and phosphoric acid whilst dicalcium phosphate dissolves as such in the beginning but readily converts to more basic forms. Thus all the three forms of calcium phosphates are inter-convertible by the hydrolysis phenomenon because monocalcium phosphate has also been found to hydrolyse into phosphoric acid and dicalcium phosphate.

1.25 gms. solid + 150 c. c. water, shaken for 2 hours.

$\text{Ca}_3(\text{PO}_4)_2$			$\text{CaHPO}_4$		
in gms. $\text{CaO}$	$\text{P}_2\text{O}_5$	Molecular $\text{CaO} : \text{P}_2\text{O}_5$	in gms. $\text{CaO}$	$\text{P}_2\text{O}_5$	Molecular $\text{CaO} : \text{P}_2\text{O}_5$
0.00924	0.01988	1.3 : 1	0.00448	0.00525	2.1 : 1
0.00672	0.01087	1.6 : 1	0.00392	0.00364	2.7 : 1
0.00644	0.01032	1.6 : 1	0.00392	0.00364	2.7 : 1
0.00560	0.00914	1.56 : 1	0.00392	0.00339	3.2 : 1
0.00560	0.00748	1.9 : 1	0.00402	0.00332	3.1 : 1
0.00504	0.00543	2.3 : 1	0.00420	0.00287	3.9 : 1

It has also been found that by adding  $\text{CaCO}_3$  to these systems the amount of phosphate in the system decreases very much. Similarly by adding basic slag containing free lime or calcium carbonate and rock phosphate containing little  $\text{CaCO}_3$ , such an effect was observed. To 1.0 gm.  $\text{P}_2\text{O}_5$  content of the phosphates of calcium and iron, 0.2 gm.  $\text{CaCO}_3$  was added and shaken with 100 c. c. water for 2 hours. The filtrates after 24 hours were analysed for their  $\text{P}_2\text{O}_5$  contents. Similarly 1 and 2 gms. of basic slag and rock phosphate were added and the amounts of  $\text{P}_2\text{O}_5$  in the extracts were determined. The results obtained clearly explain that the presence of  $\text{CaCO}_3$  or lime in any form considerably lowers the amount of phosphate in water-soluble form. This is one of the reasons why the calcareous soils are very poor in water-soluble phosphates. The calcium ions from  $\text{CaCO}_3$  or lime, due to common ion effect and a high pH, lower the solubility or suppress the hydrolysis of the phosphates.

$\text{FePO}_4$ alone	0.0041 gm. $\text{P}_2\text{O}_5$	$\text{FePO}_4 + \text{CaCO}_3$	0.000927 gm. $\text{P}_2\text{O}_5$
$\text{Ca}_3(\text{PO}_4)_2$ alone	0.0204 " "	$\text{Ca}_3(\text{PO}_4)_2 + \text{CaCO}_3$	0.00139 " "
$\text{Ca}_3(\text{PO}_4)_2$ + 1 gm. rock phosphate.	0.0200 " "	$\text{Ca}_3(\text{PO}_4)_2$ + 1 gm. basic slag.	0.00024 " "
$\text{Ca}_3(\text{PO}_4)_2$ + 2 gms. rock phosphate.	0.0184 " "	$\text{Ca}_3(\text{PO}_4)_2$ + 2 gms. basic slag.	0.00014 " "
$\text{CaHPO}_4$ alone	0.0062 " "	$\text{CaHPO}_4 + \text{CaCO}_3$	0.00008 " "
$\text{CaHPO}_4$ + 1 gm. rock phosphate.	0.0050 " "	$\text{CaHPO}_4$ + 1 gm. basic slag.	0.000064 " "
$\text{CaHPO}_4$ + 2 gms. rock phosphate.	0.0041 " "	$\text{CaHPO}_4$ + 2 gms. basic slag.	0.00004 " "

In order to imitate the above reactions in soils, 0.5 gm.  $\text{CaCO}_3$  was mixed with 25 gms. of normal soil and 0.58 gm.  $\text{Ca}_3(\text{PO}_4)_2$  was added. The contents were shaken with 150 c.c. distilled water for 2 hours and the amounts of phosphate in two successive extracts were determined by the photo-electric colorimeter using ammonium molybdate and stannous chloride to develop a blue colour.

		First extract	Second extract
Normal soil alone	...	Trace	Trace
Normal soil + 0.58 gm. $\text{Ca}_3(\text{PO}_4)_2$	...	0.638 mgms. $\text{P}_2\text{O}_5$	0.438 mgm. $\text{P}_2\text{O}_5$
Normal soil + 0.58 gm. $\text{Ca}_3(\text{PO}_4)_2$ + 0.5 gm. $\text{CaCO}_3$ .		0.445 mgm. „	0.238 mgm. „
0.58 gm. $\text{Ca}_3(\text{PO}_4)_2$ alone	...	9.000 mgm. „	5.000 mgm. „

The above results clearly show the decrease in the hydrolysis of  $\text{Ca}_3(\text{PO}_4)_2$  when it is mixed with the soil and the hydrolysis is further checked when  $\text{CaCO}_3$  is added to the soil. It seems, therefore, that the presence of  $\text{CaCO}_3$  in the system greatly influences the hydrolysis of calcium phosphates in the soil. This is probably one of the chief reasons why the water extracts of the soils are poor in soluble phosphates. A concentration of phosphate equal to 0.445 mgm. of  $\text{P}_2\text{O}_5$  per 25 gms. of soil corresponds to 39.8 lbs. of  $\text{P}_2\text{O}_5$  per acre, obtained by the addition of  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{CaCO}_3$  to the soil. This amount is greater than the amounts of phosphate usually present in the soil extracts. Hence it seems that if the phosphate is present as  $\text{Ca}_3(\text{PO}_4)_2$  in the soil and even if  $\text{CaCO}_3$  exists in the free state in soils, appreciable amount of phosphate should be present in the water extracts but as there is practically no phosphate in the water extracts of the normal soil, it seems that  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{CaCO}_3$  might form some more insoluble basic phosphates like the hydroxy-apatite or carbonate-apatite. On ageing, tricalcium phosphate may become inactive. If  $\text{CaHPO}_4$  is more stable than  $\text{Ca}_3(\text{PO}_4)_2$ , it should exist as such in the soil but its solubility is greatly affected by the presence of  $\text{CaCO}_3$  as shown by us earlier in this paper, smaller amounts of phosphate ions are likely to be present in the soil solution even if it contains  $\text{CaHPO}_4$  as such. Boischo<sup>55</sup>, Basett<sup>56</sup>, Cole and Olsen<sup>57</sup> and MacIntire and Shaw<sup>58</sup> support the existence of  $\text{CaHPO}_4$  in presence of a large excess of  $\text{CaCO}_3$ . The latter workers<sup>59</sup> have postulated that when superphosphate is added to calcareous soils or soils to which lime has been added,  $\text{CaHPO}_4$  is formed which persists in the soil unchanged. The excess of calcium carbonate in course of time converts it into tricalcium phosphate. McGeorge and Breazeale<sup>60</sup> found that in calcareous soils of Arizona the soluble phosphates form phosphates of varying degree of solubility. The more insoluble phosphates proposed by Lewis, Baker and Synder<sup>61</sup> and McGeorge and Breazeale<sup>62</sup> are carbonate-apatite. Cole, Olsen and Scott<sup>63</sup> have shown that at high concentrations of  $\text{K}_2\text{HPO}_4$  solution, precipitation of dicalcium phosphate takes place, while at low concentrations of phosphate, a rapid mono-layer adsorption on  $\text{CaCO}_3$  surface takes place. The initial products of these reactions are characterized by very high specific surfaces and greater phosphate solubility than the stable hydroxy-apatite or fluorapatite. We have found that when  $\text{CaCO}_3$  is treated with M/100 or M/500  $\text{Na}_2\text{HPO}_4$  solution, and is subsequently leached with water for 7-8 times, there is only a trace of phosphate left in the washed residue of  $\text{CaCO}_3$ . We have also found that from the soils treated with  $\text{Na}_2\text{HPO}_4$  or monocalcium phosphate, fair amounts

of phosphate can be detected in 8th extract with water. To 25 gms. of soil 150 c.c. of the phosphate solution were added and the treated soils were washed repeatedly with 150 c.c. water and the  $P_2O_5$  in the 8th extract was determined and calculated in lbs./acre in the following table :—

Treated soils	M/100 $Na_2HPO_4$	M/100 $CaH_4(PO_4)_2$	M/500 $CaH_4(PO_4)_2$
	$P_2O_5$ in pounds per acre in 8th. water extract.		
Good soil	91.6	270.0	85.8
Normal soil	28.5	85.8	28.5

The above results explain the residual effect of superphosphate in soils. It has been reported by Aslying<sup>64</sup> that meta-stable octo-calcium phosphate [ $CaH_4H(PO_3)_3$ ] is formed in Rothamsted soils containing  $CaCO_3$  where large quantities of Superphosphate is applied. At higher pH values, hydroxyapatite may also be formed though the process is very slow but a continuous release of phosphate ions from the superphosphate-treated soils indicates the presence of  $CaHPO_4$  in a freshly precipitated condition which is more soluble than the octo-phosphate or hydroxyapatite. With the lapse of time the ageing of the finely divided phosphate may take place and hence the solubility gradually decreases.

In soils rich in organic matter there is always a liberation of  $CO_2$  which after being dissolved in soil-water exerts a dissolving action on the calcium phosphates present in the soils. McGeorge<sup>65</sup> has found that the solubility of phosphates in alkaline soils is increased with increase in the concentration of  $CO_2$ . It has been observed by us that when  $CO_2$  is blown into the suspensions of  $Ca_3(PO_4)_2$ ,  $CaHPO_4$  or basic slag or rock phosphate, there is always an increase in the phosphate contents of the filtrates as is recorded in the following table :—

↓ gm.  $P_2O_5$  + 200 c.c. water and  $CO_2$  passed for 2 hours.

	with water ( $P_2O_5$ in gms.)	with water in which $CO_2$ was blown. ( $P_2O_5$ in gms.)
$Ca_3(PO_4)_2$	0.02217	0.0230
$CaHPO_4$	0.0063	0.0075
Basic slag	0.00007	0.0001
Rock phosphate	0.00008	0.0001

The above results show why greater amounts of phosphate exist in the extracts of soil, rich in organic matter, because  $CO_2$  has got a solvent action on the calcium phosphates by converting them to more soluble forms as pointed by Dhar. Hence the good soil which contains 1.4% C and 0.41%  $P_2O_5$  loses more phosphate in comparison with the normal soil which contains 0.4% C and 0.079%  $P_2O_5$  though the former contains 4%  $CaCO_3$  whilst the latter only 1%.

It has been reported in U. S. A. that the areas of soil richest in phosphorus occur in the limestone belt of Kentucky where the soils are known to contain well

ever 10000 lbs. per acre and those lands are fertile and maintain their fertility for a long time. Arrhenius<sup>66</sup> has observed that soils near human habitations, past or present, in different parts of Sweden and Java are richest in phosphate and fertile. Similar results have been recorded in the neighbourhood of cities in Denmark. Hinkle<sup>67</sup> showed by chemical analysis that calcareous soils are well supplied with total phosphorus but available phosphate was small. Recent results from Idaho University indicates that though there is reduction in available phosphorus when phosphate fertilizer is applied to calcareous soils, the succeeding crops utilize a great deal of fixed phosphate, hence P-fixation is not so marked in calcareous soils as in acid soils. Collins<sup>68</sup> reports that most nutritious pastures in England and best dairy pastures in France are those that are rich in phosphates. All these facts support the view point that calcium carbonate and phosphate conserve each other and that the phosphate status of soils determines their fertility level as postulated by Dhar.

#### SUMMARY

The amount of phosphate present in the water-extract of different soils depends upon :

- (a) Soil-water ratio,
- (b)  $\text{CaCO}_3$  content,
- (c) Soluble salts present,
- (d) Organic matter content,

and (e) Original phosphate status of soils.

A good soil, rich in organic matter and phosphate, loses a great deal of phosphate, while a soil poor in these constituents loses a small amount of phosphate on leaching with water. The amount of phosphate increases when the soils are washed with dilute salt solutions of sodium and potassium. The addition of  $\text{Ca}_3(\text{PO}_4)_2$  to soils, due to its hydrolysis increases the concentration of phosphate ions in the water extracts of the soils but  $\text{CaCO}_3$ , which checks the hydrolysis, reduces their amounts. The successive liberation of phosphate from soils to which monocalcium phosphate or  $\text{Na}_2\text{HPO}_4$  has been added indicates the formation of reactive  $\text{CaHPO}_4$  in very finely divided state in soils.

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# EFFECT OF PHOSPHATES ON MICROBIOLOGICAL ACTIVITIES IN SOILS

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Decomposition of organic matter in soils is mostly a microbiological process accompanied by several important changes in carbon and nitrogen which are related to soil fertility. Along with the oxidation of organic carbon ultimately to form  $\text{CO}_2$ , evolution of which from a soil had been considered as an index of microbiological activity (Russel and Appleyard 1915; Stoklassa 1922; Andrews 1934), organic nitrogen is oxidised in different stages by distinct microbiological processes. Some important groups of soil microorganisms also utilise the energy of oxidation of organic carbon for fixation of atmospheric nitrogen which result in an increase in nitrogen content of soil.

It is well known that phosphorous is an essential constituent of microbial cells and it would appear that sufficiency or deficiency of the same in a soil would affect the development and activity of different soil microorganisms. Stimulation of decomposition of organic matter and therefore, of evolution of  $\text{CO}_2$  from soil by addition of phosphates had been observed by many workers (Fred and Hart 1915; Waksman and Starkey 1924). Increase in nitrification in various degrees in soil due to addition of phosphates was also noted (Peterson and Scott 1913; Fraps 1920; Whiting and Scoonover 1923; Brown and Gowda 1924; Fraps and Sterges 1938). Christensen (1921) showed that basic content of lime and phosphoric acid determined the speed at which nitrogen fixation took place. This view was subsequently confirmed by other workers (Waksman and Karunakar 1924).

During the present investigations, the effect of addition of different phosphates like superphosphate, bone meal, Singbhum phosphate and Trichi nodules on the evolution of  $\text{CO}_2$ , rate of nitrification and nitrogen fixation has been studied in a sandy loam of almost neutral reactions in a calcareous and in an acid soil. In addition to these, studies were made on the evolution of  $\text{CO}_2$  and nitrification with the addition of mustard cake and on nitrogen fixation with the addition of mannite. Effect of neutralisation of the acid soil by addition of lime on these processes was also noted down. It was expected that the data would throw considerable light on the precise changes in different microbiological processes in the soil as a result of incorporation of phosphate in different forms.

## MATERIALS AND METHODS

*Soils.*—Surface soils (0-9") from Delhi, Pusa and Ranchi were air dried and sampled through a 2 m.m. sieve. The composition of the soils is given in the Appendix I.

*Phosphates.*—Superphosphate, bone meal, Singbhum phosphate and Trichi nodule were used in the experiments. The composition of the phosphates is given in the Appendix II.

*Methods.*—Addition of phosphates to the soils was made at the rate of 10 mg of total  $\text{P}_2\text{O}_5$  per 100 gms of soil. In the  $\text{CO}_2$ -evolution and nitrification studies mustard cake containing 30 mg of nitrogen was added to 100 gm lots of soil. In

the nitrogen fixation studies, 1 gm of mannite per 100 gms of soil was used as a source of energy material, and in neutralisation of Ranchi soil, 1 gm of  $\text{CaCO}_3$  was added to each 100 gm lots of Ranchi soil. In all the studies, the soil with the added material was moistened to one third its saturation capacity and incubated at  $30^\circ\text{C}$ .

The analysis of the soils was carried out by the usual methods (Piper 1942). Total nitrogen in the soils was estimated by Kjeldahl-Gunning's method (A. O. A. C. 1946).  $\text{CO}_2$  evolution in soils was measured by the method of Pettenkoffer (1858). For nitrite nitrogen the method of Greiss-Illosvay and for nitrate that of Charcot and Priatt (Wright 1934) were followed with a photoelectric colorimeter (Lumetron Model 402-E).

#### RESULTS

Average amounts of  $\text{CO}_2$  evolved from the different soils under different treatments are given in Table I,

TABLE I  
 $\text{CO}_2$  evolved in ten days from soils under different treatments (mg per cent).

Treatments		Without mustard cake	With mustard cake
<i>Delhi soil</i>			
Control	...	58.76	238.15
Superphosphate	...	76.40	291.94
Bone meal	...	71.60	271.12
Singbhum phosphate	...	71.24	261.80
Trichi nodule	...	71.12	250.44
<i>Pusa soil</i>			
Control	...	70.62	345.70
Superphosphate	...	87.12	371.88
Bone meal	...	79.66	361.28
Singbhum phosphate	...	79.82	359.74
Trichi nodule	...	75.72	357.56
<i>Ranchi soil</i>			
Control	...	34.76	231.12
Superphosphate	...	52.40	299.34
Bone meal	...	50.57	265.70
Singbhum phosphate	...	46.40	255.10
Trichi nodules	...	40.70	250.58
<i>Ranchi soil with lime</i>			
Control	...	138.04	428.44
Superphosphate	...	191.39	547.96
Bone meal	...	150.67	515.53
Singbhum phosphate	...	147.30	514.11
Trichi nodule	...	149.70	500.64

Average amounts of nitrite and nitrate nitrogen formed in the soils under different treatments in ten weeks are given in Table II.

TABLE II  
Nitrification in soils under different treatments during 10 weeks  
NO<sub>2</sub>-N and NO<sub>3</sub>-N are in mg per cent

Treatment	Without mustard cake		With mustard cake	
	NO <sub>2</sub> -N	NO <sub>3</sub> -N	NO <sub>2</sub> -N	NO <sub>3</sub> -N
<i>Delhi soil</i>				
Control	...	0.47	4.90	5.50
Superphosphate	...	0.38	5.40	0.69
Bone meal	...	0.38	5.60	0.42
Singbhum phosphate	...	0.49	5.50	0.60
Trichi nodule	...	0.40	5.40	0.79
<i>Pusa soil</i>				
Control	...	—	5.55	—
Superphosphate	...	—	5.60	—
Bone meal	...	—	5.40	—
Singbhum phosphate	...	—	5.30	—
Trichi nodule	...	—	5.20	—
<i>Ranchi soil</i>				
Control	...	—	3.02	—
Superphosphate	...	—	3.80	—
Bone meal	...	—	3.60	—
Singbhum phosphate	...	—	3.54	—
Trichi nodule	...	—	3.02	—
<i>Ranchi soil with lime</i>				
Control	...	—	6.40	—
Superphosphate	...	—	7.70	—
Bone meal	...	—	7.30	—
Singbhum phosphate	...	—	7.20	—
Trichi nodule	...	—	7.10	—

Average amounts of nitrogen fixed in the soils under different treatments during a periods of ten weeks are given in Table III.

TABLE III  
Nitrogen fixation in soils treated with different phosphates during ten weeks  
(mg. per cent.)

Treatment	Without mannite	With mannite
<i>Delhi soil</i>		
Control	4.20	9.20
Superphosphate	6.60	15.60
Bone meal	6.20	14.14
Singbhum phosphate	6.20	13.30
Trichi nodule	5.60	13.30
<i>Pusa soil</i>		
Control	6.02	11.60
Superphosphate	7.80	16.00
Bone meal	7.72	15.40
Singbhum phosphate	6.12	14.90
Trichi nodule	6.16	14.40
<i>Ranchi soil</i>		
Control	2.10	2.50
Superphosphate	2.70	3.50
Bone meal	2.50	3.40
Singbhum phosphate	2.30	3.20
Trichi nodule	2.30	3.20
<i>Ranchi soil with lime</i>		
Control	4.00	4.50
Superphosphate	7.20	9.10
Bone meal	5.00	8.70
Singbhum phosphate	5.00	7.00
Trichi nodule	5.00	7.00

#### DISCUSSION OF RESULTS

From the data in Table I it is seen that incorporation of phosphates increases the microbiological activity of the soil as reflected in the evolution of  $\text{CO}_2$  and when organic matter like mustard cake is added to the soil there is much larger

evolution of  $\text{CO}_2$ .  $\text{CO}_2$  evolution in the soils, however, differ in their response to treatment with phosphates, when no organic matter is added. This response is quite appreciable in Delhi soil and is much less in the soil from Pusa. Phosphates also differ in their utilisation by microorganisms. Superphosphate causes the highest evolution of  $\text{CO}_2$  and it may be due to the larger amount of water soluble  $\text{P}_2\text{O}_5$  contained in it as compared with the other phosphates. The differences in increases in evolution of  $\text{CO}_2$  due to treatments of phosphates are so small in Delhi soil that different phosphates may be utilised with almost equal efficiency while this is not true in the other soils.

Nitrification in Delhi soil is enhanced by treatments with phosphates but not to a very remarkable extent even when a readily nitrifiable organic matter like mustard cake is added to it. In Pusa soil, the effect is not noticeable; there are, in some cases, decreases in nitrification. In the acid soil from Ranchi, with and without any treatment with organic matter a similar trend is observed. Nitrification of mustard cake in the Ranchi soil is however, increased due to addition of phosphates particularly with superphosphate whether the soil is treated with lime or not. Increase in nitrification when lime is added is quite pronounced.

There is increase in nitrogen fixation in the soils as a result of addition of phosphates, though under acid conditions of Ranchi soil it is not appreciable even with mannite (Table III). Neutralisation of the acidity with lime makes these increases in nitrogen fixation in Ranchi soil significant. Highest increase is observed invariably with superphosphate in all the cases and in cases of almost neutral and calcareous soils which have generally a low nitrogen and organic matter content when they are treated with an energy material like mannite.

#### SUMMARY AND CONCLUSIONS

During the present investigation, the effect of addition of superphosphate, bone meal, Singbhum phosphate and Trichi nodule on  $\text{CO}_2$  evolution, nitrification and nitrogen fixation had been studied in an almost neutral, in a calcareous and in an acid soil. The same had also been studied with added organic matter, mustard cake in the  $\text{CO}_2$  evolution and nitrification and mannites in nitrogen fixation and in addition to these, in the case of the acid soil, with the addition of lime to neutralise the acidity.

Addition of phosphates appreciably enhanced evolution of  $\text{CO}_2$  from soils with or without the treatment with organic matter. No appreciable increase in nitrification was, however, noted due to incorporation of phosphates with soil.

Phosphates increased nitrogen fixation in soils which were neutral or alkaline. The effect was insignificant in acid soils. If, however, the acidity was neutralised with lime, increase in nitrogen fixation due to treatments with phosphates became appreciable.

Though increases in  $\text{CO}_2$  evolution, nitrification and nitrogen fixation in soil were highest under treatment with superphosphate, the differences in the same, due to treatments with other phosphates were not high, showing thereby that these indigenous phosphates could be used with fair efficiency for improvement of soil fertility.

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## APPENDIX I

### *Composition of the soils*

Constituents expressed as per cent on moisture free basis.

Constituents		Delhi soil	Pussa soil	Ranchi soil
Coarse sand	...	25.10	2.90	9.20
Fine sand	...	22.60	10.20	24.49
Very fines and	...	8.60	23.05	20.27
Silt	...	23.00	21.60	20.40
Clay	...	19.20	8.80	21.20
pH	...	7.4	8.4	5.9
				8.1 (with lime)
Saturation capacity	...	36.9	48.0	32.0
CaCO <sub>3</sub>	...	—	30.94	—
Organic carbon	...	0.34	0.25	1.07
Organic nitrogen	...	.048	.036	.088
Nitrite nitrogen (mg)	...	tr	tr	tr
Nitrate nitrogen (mg)	...	.60	.65	.34
CaO	...	.56	17.47	.22
P <sub>2</sub> O <sub>5</sub>	...	.08	.12	.19

## APPENDIX II

### *Composition of the phosphates*

Constituents expressed as per cent. on moisture free basis

Phosphate		Total N	Total P <sub>2</sub> O <sub>5</sub>	Water soluble P <sub>2</sub> O <sub>5</sub>
Superphosphate	...	0.60	15.30	11.60
Bone meal	...	3.74	23.20	0.39
Singbhum phosphate	...	0.40	21.90	.27
Trichi nodule	...	.10	21.60	.23



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# PHOSPHATE MANURING IN JUTE

By

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Jute plant, from the point of view of fibre production is reported to respond to nitrogenous fertilisers most. It has already been reported that phosphates as superphosphate when applied with nitrogen, though often do not contribute to the increase in the fibre production, improve the fibre quality.

In the present investigation results of the combinations of different levels of nitrogen as ammonium sulphate with phosphate as superphosphate were studied, starting from very low to very high doses of the both.

TABLE—I

Treatments		Yield per acre in lbs.		Green Wt.
P <sub>2</sub> O <sub>5</sub>	N <sub>2</sub>	Green Wt.	Fibre Wt.	Fibre Wt.
0	0	33069	2199	15.03
10	0	25519	1664	15.33
10	15	35938	2350	15.29
10	20	35636	2368	15.05
10	25	34881	2476	14.09
10	30	38052	2451	15.52
20	0	38203	2475	15.44
20	30	38958	2597	15.00
20	40	41525	2611	15.90
20	50	40317	2605	15.47
20	60	38354	2596	14.77
40	0	22046	1700	12.96
40	60	39411	2735	14.41
40	80	42280	2869	14.73
40	100	40317	2740	14.35
40	120	46961	3043	15.43
80	0	32163	2147	14.98
80	120	43337	2695	16.08
80	160	42129	2600	16.20
80	200	40468	2584	15.66
80	240	41827	2655	15.75
160	0	35183	2331	15.09
160	240	45300	2991	15.14
160	320	46508	2775	16.75
160	400	43488	2457	17.69
160	480	35334	2190	16.13

It is seen from Table I that if superphosphate is added alone, the fibre yield is depressed markedly, the yield is however gradually increased with further additions of superphosphate but it is always less than or same as in control.

But superphosphate in combination with nitrogen, gives definite response when the ratio of phosphate : nitrogen is between 1:1.5 to 1:2.

In a previous experiment it was found as will be seen from the following table (Table II) that quantity of fibre obtained per unit of green matter progressively increased with phosphates but though at first it increased with the first dose of nitrogen, later on it gradually decreased.

TABLE—II

Treatment	Gms. of fibre/lb. of Green Wt.
0 lb. $P_2O_5$	30.907
20 " "	32.709
40 " "	33.723
60 " "	35.242
80 " "	35.841
0 " $N_2$	29.346
25 " "	33.383
50 " "	32.966
75 " "	31.562
100 " "	30.562

From Table I it may be seen that in many cases nitrogen in combination with superphosphate has not increased the quantity of green matter in proportion with the fibre.

The analysis of the plant shows that jute requires a considerable amount of phosphorus. Sengupta (1953) has shown that of the major plant nutrients absence of P produced the most adverse effect. Superphosphates, as have been shown reduces the fibre yield though improving quality [Kundu, Mukherjee, Rao and Chakravorty (1956)]. In order to test it in further detail a pot experiment was designed to see the effect of different sources of phosphate, such as superphosphate (single), sodium phosphate (monazite source), calcium phosphate (tri), potassium phosphate, Basic Slag, Bone Meal etc., in jute. The data are given in Table III.

TABLE—III

Treatments		Yield per plant in gms.		
$P_2O_5$ on 40 lbs. per acre		Green Wt.	Stripped Wt.	Seed Wt.
Superphosphate	...	101	66	1.2
Sodium phosphate (Monazite)	...	186	131	7.0
Calcium phosphate (Tri)	...	171	121	7.7
Potassium phosphate	...	369	236	15.0
Basic Slag	...	180	114	5.8
Bone Meal	...	388	256	13.7
Control	...	122	74	6.3

It may be seen from above that all other phosphates except super phosphate gives better results. It is also seen from the Table III phosphates except super-phosphate not only gives good yield of crop but also gives better yield of seed. It may be stated, therefore, that though superphosphate has got depressing effect on crop yield, other phosphate may be beneficial. It may also be seen from Table III that potassium phosphate and Bone Meal give the best results both for fibre production as well as for seed yield.

Our sincerest thanks are due to Dr. B. C. Kundu, M.A., Ph.D., F. N. I., F. L. S., Director, Jute Agricultural Research Institute, for his kind interest and help during the progress of the work.

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# A METHOD OF SEPARATION AND IDENTIFICATION OF INOSITOL PHOSPHATES OF SOIL BY ANION EXCHANGE CHROMATOGRAPHY

By

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The surface layers of the soils contain a fairly good amount of organic phosphorus was shown by a number of workers. (1, 2, 3, 8, 9, 17, 23, 26, 27, 28). The major portion of these organic phosphorus compounds is represented by phytin and other inositol phosphates (2, 8, 9, 21, 24 & 31). The various inositol phosphates are a good source of available phosphorus to plants in soils. (2, 4, 6, 9, 11, 12, 16, 19, 22, 23, 29 and 30). Recently much stress has been laid upon the importance of these types of phosphates in soil and plant relationships. The relative availability of various inositol phosphates has been shown to vary due to the easy hydrolysis of mono, di and triinositol phosphates (21).

It, therefore, seems that the evaluation of various forms of inositol phosphates and their quantitative determination is essential for the proper assessment of available phosphorous status of a particular soil. Smith has recently developed a chromatographic method for the separation of inositol phosphates. The characteristic inositol/phosphate ratio was taken as an index to particular compound. Smith and Clarke applied this method to extracts of organic phosphorous compounds from soils. In their method they collected the liquid coming out of the column during definite intervals and then determined the phosphorus content. The phosphorus content was plotted against time. The peaks in the graph represented various compounds. The entire method takes nearly ten days to be completed.

In the present paper authors have presented a method which takes comparatively much less time and is relatively easier to handle.

## METHODS AND MATERIALS

**Preparation of anion exchange resin.**—Aniline and hydrochloric acid are mixed in equal proportion and then a 7.5% solution of urea in water is added. Formalin is then added and after nearly 12 hours, gel is precipitated out by addition of formaldehyde. The gel is then dissolved in 20% hydrochloric acid and Aniline hydrochloride and formaldehyde are added to precipitate out the final resin. The resin is treated with alkali and then dried (7).

**Preparation of sodium phytate and sodium phytate derivatives.**—It was done according to technique suggested by Jackman and Black (14, 15 and 25).

**Extraction of inositol phosphates from Farm Yard Manure**—It involved the following steps :—

- (a) Leaching with 1% hydrochloric acid solution.
- (b) Extraction with  $N/2$  Na OH solution at 90° C.

- (c) Precipitation of bulk of organic matter at Ph 1.
- (d) Precipitation of lead salt in 10% acetic acid.
- (e) Treatment with  $H_2S$  to liberate the inositol phosphates.
- (f) NaOBr oxidation.
- (g) Lead salt precipitation in 10% acetic acid.
- (h) Decomposition with  $H_2S$  and then precipitation of calcium salt by  $CaCl_2$  and NaOH.
- (i) Filtrate of calcium salt subjected to Phosphorus determination for Inositol mono phosphate and then precipitation of lead salt.
- (j) Lead salt decomposition by  $H_2S$ .
- (k) Removal of excess  $H_2S$  by aspiration.

**Estimation of organic phosphorus**—It was done by the method as outlined by Pearson. The final colour development for determination of inorganic phosphorus was done by the technique of Dickman and Bray. The determination of inositol was done by Young's Iodomercurate Method. (5, 8, 9, 10, 18, 20, 21, 31 and 32).

100 gms of Farm yard Manure sample collected from Banares Hindu University Farm, having 0.26% total phosphorus upon extraction gave inositol phosphates equivalent to 68 mgms of P.

1 Kgm of soil from Shahanshahpur (Banaras) having 0.143% Org P gave inositol phosphates upon extraction equal to 40 mgms P.

200 mgms of inositol phosphate derivatives were prepared from phytin extracted from rice bran. (25)

**Development of Chromatogram**—Three columns of anion exchange resin were made in three tubes of different dimensions with cotton wool at the bottom of the tube. Each tube had a stop-cock at its lower end, and a side stop cock and a central tube at the upper end. The three tubes holding the columns were connected to each other by rubber tubing. The level of each tube was adjusted so that liquid from previous tube could flow into the other tube. The first tube was attached to reservoir containing a displacing solution of N/100 HCl. The solution containing inositol phosphates (nearly 10 c.c.) was poured cautiously at the top of first column and the level of liquid was then maintained with water in two remaining columns. First column is then connected to displacing solution of N/100 HCl and the rate of flow of liquid is adjusted to 4-5 drops per minute. The displacement is allowed to continue. The liquid coming out of the columns is collected after every six hours and the determination of P was carried out. After 48 hours, the columns are taken out and each one of them is treated with a saturated solution of lead acetate in 15% acetic acid under pressure. The columns are then washed with distilled water free from  $Co_2$ , till no trace of lead could be detected in washings even by Colorimetric tests. Now the columns are connected to the kipp's apparatus from where a supply of pure  $H_2S$  gas was drawn. After nearly 10 minutes of slow suction the columns are taken off. The columns now show definite rings which are shaded slightly black. Rings are then cut off from the columns from points from where they start, dispersed in water and  $H_2S$  passed. The entire thing is then filtered, raised to definite volume and inositol/P ratio is determined.

## RESULTS AND DISCUSSION

Inositol phosphates equivalent to 60 mgms of P from Sodium phytate derivatives gave 4 rings with inositol/P ratio .962, 1.140, 1.42, 1.880, respectively, representing Hexa, penta, tatra and tri derivatives of inosital phosphates.

In farm yard manure extract, representing 60 mgms of inositol phosphate P, 3 rings were seen after chromatographic separation which represented Hexa, penta, and tetra phosphates. The inositol/P ratios were 0.964, 1.132 & 1.394 respectively.

The extract of inositol phosphates from soil containing 25 mgms of P., upon chromatographic separation, gave two distinct rings, in which the inositol/P ratios were 0.962 and 1.104 respectively. There were, however, two more rings but the phosphorus present therein was too small to make any significant quantitative determination of inositol.

TABLE No. I

	Sod Phytate derivatives			Farm Yard manure			Soil		
	Mgms of inositol P	Mgms of inositol	Inositol /P	Mgms of inositol P	Mgms of inositol	Inositol /P	Mgms of inositol P	Mgms of inositol	Inositol /P
First ring ...	32.17	31.08	0.968	42.83	41.31	0.964	18.32	17.63	0.962
2nd ,, ...	16.71	18.93	1.133	10.91	12.33	1.131	5.08	5.61	1.104
3rd ,, ...	5.81	8.27	1.423	6.13	8.539	1.394	0.96	...	...
4th ,, ...	3.23	6.16	1.880	...	...	...	0.34	...	...

The results indicate that the method gives a separation of various inositol phosphates. In sodium phytate derivatives separation into four rings is very distinct. Similarly, Farm yard manure and soil extracts also gave 3, and 4 rings respectively. The inositol/P ratio are also quite characteristic for various compounds.

This method is based on the fact that all inositol phosphates are precipitated out on a resin as their lead salt if a saturated solution of lead acetate in 10% acetic acid is added (13). The precipitated product becomes immobile. The  $H_2S$  gas is used to indicate the position of these compounds which are precipitated out on the resin.  $H_2S$  produces a black precipitate of lead sulphide and liberates the inositol phosphates. The black portion indicates the exact position where the phosphates are lodged and therefore, cutting out of resin at those positions enables a separation of various phosphates. The inositol/P ratio can then be determined by completely precipitating out the lead, removing it and then carrying out estimates of Inositol and phosphate in the filtrate thus obtained. This method can be completed in nearly 3 days time.

## SUMMARY

A chromatographic method for the separation and identification of inositol phosphates in soils and farm yard manure is described. Use is made of the fact that lead acetate in 10% acetic acid solution precipitates out all inositol phosphates on the resin. The position of these lead salts can be detected by passing  $H_2S$ . This enables determination of inositol/P ratio and thus a direct identification of various inositol phosphate compounds is possible. Farm yard manure was found to contain Hexa, penta, and tetra forms; whereas soil showed Hexa and penta inositol phosphates as major constituents. There were, however, two other forms in soil in very small concentrations, whose exact composition could not be determined.

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# A STUDY OF PHOSPHORUS-NITROGEN RELATIONSHIP IN SAGAR SOILS

By

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The potash content in soils is definitely more abundant all over the world than the phosphate or nitrogen content. On the other hand, the nitrogen content in temperate climate is definitely higher than the phosphate content. It is stated that the phosphate content of soils can vary from 0.3—0.0% while the nitrogen content from 3.0—0.4%. It has been reported that the nitrogen content of fen soils can be as high as 3%, the soils being fairly rich in phosphate content. Sir John Russell<sup>1</sup> seems to be quite justified when he states that phosphates applied to soils may determine the course of history, even in the near future, specially in the cold and wet countries.

In tropical countries with a moderate amount of rainfall, the  $P_2O_5$  content of soils is usually double or slightly more than the nitrogen content. In alluvial soils the nitrogen content is approximately 1,100 lbs. per acre, i.e., approximately 0.04—0.05%, while the  $P_2O_5$  content is 0.1%, i.e., 2,000 lbs. per acre<sup>2</sup>. There seems to be a fundamental difference between the soils of temperate and tropical countries, the nitrogen content of former being higher than the  $P_2O_5$  content.

It is no wonder, therefore, if it is presumed that the phosphate is responsible to a great extent for the nitrogen content as has been observed by several workers. Bear<sup>3</sup> has gone to the extent of saying that phosphate fertilizers together with potash salts and lime, within limits can be substituted for nitrogen fertilizers. The activity of both, the symbiotic and the non-symbiotic bacteria, is stimulated to a greater activity in presence of the former. The rank growth of white clover on addition of phosphate and potash resembles that with nitrogenous fertilizers. Dhar<sup>4</sup> also is of the opinion that phosphates play vital role in the improvement and maintenance of soil fertility. Russell<sup>5</sup> has clarified the above statement by presuming that the proteins that are present in soil humus are likely to be stabilised by the formation of nucleo-proteins, phospho-proteins etc. in soil, when a phosphate is present in the system.

It has been postulated that the plant residue or other organic matter in the soil undergoes slow oxidation and fixes nitrogen of air, more in presence of calcium phosphate, rock phosphate, basic slag or bone meal than in absence<sup>6</sup>. The neutral fen soils of England have been found rich in nitrogen to the extent of 3%. And the muck soils of New Jersey contain 2.7% of nitrogen in the top 12" layer of the soil. The soils have been found to contain 0.2% of  $P_2O_5$ .<sup>7</sup> Dhar<sup>8</sup> has, therefore, very strongly advocated that the phosphate status of a soil usually determines its nitrogen status, and consequently the reproductive potential in the following lines:

"From a survey of soils of different countries, it appears that the nitrogen status of a soil is intimately connected with the phosphorus status all over the world. When the  $P_2O_5$  content is 1,000 lbs. per acre, the nitrogen content cannot be greater than 0.1%, but when  $P_2O_5$  content become 2,000 lbs. or more, the nitrogen content can go upto 0.2% or more. In other words, as the  $P_2O_5$  content of the soil increases, there is a marked increase of its nitrogen content. As a matter of fact the increase of nitrogen content appears to be more steep with increasing amounts of  $P_2O_5$  content in the soils".

In view of the above facts, 26 soil samples in and around Sagar were collected and their chemical constitution were studied in details in an attempt to group them as "good, normal and inferior" soils with respect to their phosphate and nitrogen contents, in harmony with the common vegetation and yield in cultivation in the surrounding areas.

### EXPERIMENTAL

The collection and sampling were carried with the following main considerations :—

(1) The soil sample distinctly belongs to a different type with regard to the physical conditions, colour, nature and density of vegetation and the annual produce of crops in the adjoining fields.

(2) The sample was a representative of the area, so far as possible.

(3) Composite samples were collected with the help of a spade at different places (six spots) of the area, after removing the first six inches layer of soil containing vegetation, main parts of the roots and the other incidental additions of the foreign matter.

(4) Uncultivated, virgin soils lying near cultivated fields were sampled.

The summary of the results of analysis of the twenty six soil samples with special reference to  $P_2O_5$  and nitrogen content and their grouping are shown in table 2, page 450.

### DISCUSSION

J. S. Burd<sup>9</sup> has recognised soil as good and inferior with regard to their usefulness in determining either, the present or potential productivities, and the comparative amounts of plant food materials that are found by different methods of soil analysis. It is important to note in this connection that both the good and poor soils chosen by him and those collected at Sagar, have been found to differ considerably in the nutrient contents of their water extracts, even though the total amounts of several oxides of which they contain, may be sufficiently high, and also similar in many soils, as is clear in the following table:

TABLE No. 1

	K <sub>2</sub> O%	CaO%	MgO%	P <sub>2</sub> O <sub>5</sub> %	NO <sub>3</sub> %
Good Soil :—					
(a) Complete analysis (fusion)	1.98	1.48	2.66	0.23	...
(b) 1—Acid digestion (1.115% HCl)	1.05	1.43	2.46	0.22	...
2—Acid extraction (1% citric acid) ...	0.04	0.45	0.22	0.10	...
3—Water extraction (p.p.m.)	57	127	40	12	146
Poor Soil :—					
(a) Complete analysis (fusion) ...	1.85	1.50	3.57	0.21	...
(b) 1—Acid digestion (1.115% HCl)	0.89	1.48	3.32	0.20	...
2—Acid extraction (1% citric acid) ...	0.04	0.42	0.14	0.07	...
3—Water extraction (p.p.m.)	52	45	23	5	88

Moreover, the information gathered about Sagar soils from the local areas discloses that with irrigated wheat, the combination of inorganic nitrogen and phosphate gave best increases in yields. Thus, all soils respond to nitrogen and mainly to phosphate, so much so, that the present problem of manuring in India concerns, in main, the phosphate status of soils. The proper application of phosphates, therefore, which chiefly builds up the soil fertility, is an important aspect of increasing the productivity by which the farmer may derive both long and short term benefits.

The analytical data of Sagar soils from various places, in and around Sagar reveals the fact that the above statement can also be applicable to these soils—that the range of P<sub>2</sub>O<sub>5</sub> content varies between 0.4006% and 0.0212% of the oven dried soils; it has also been found that the soils rich in phosphate content are rich in nitrogen content i.e., the soils containing 0.4006% of P<sub>2</sub>O<sub>5</sub> gave on analysis 0.2026% of nitrogen, while the soils containing 0.0212% of P<sub>2</sub>O<sub>5</sub> gave 0.0325% of nitrogen, the intermediate values lying in between. With this data, we have arrived at the conclusion that the Sagar soils stand in close agreement with the above observations. The information gathered from the local areas also discloses that the vegetation and the reproductive potential of the area adjoining the sampling spot, is also governed by the phosphate—nitrogen explanation i.e., the soils rich in phosphate and nitrogen have been found to be richer in vegetation and yields of cultivation than those, which are poor.

An attempt has therefore been made here to group the soils, collected from various places in Sagar district into three categories as “good, normal and inferior” on the basis of the analytical data of the phosphate and the nitrogen content. The soils containing 0.0—0.0700% of P<sub>2</sub>O<sub>5</sub> are termed as inferior, those containing above 0.0700—0.2000%, as normal and those having above 0.2000% as good soils. The

samples, therefore, numbering 1, 2, 3, 5, 7, 8, 11, 12, 13, 15, 16, 17, 25 and 26 fall under the category of inferior soils, 4, 2, 20, 21, 22 and 14 under normal and 6, 10, 18 19 and 23 under good soils, when they are placed in increasing order of their  $P_2O_5$  content, in table No. 2 below.

TABLE No. 2

Sample Nos.	$P_2O_5$ content%	Nitrogen content %	$P_2O_5/N$ ratio	Water Extraction %	Category
1	0.0693	0.0593	1.17	0.1403	INFERIOR
2	0.0448	0.0468	0.96	0.1441	
3	0.0247	0.0322	0.77	0.1159	
5	0.0518	0.0495	1.05	0.1027	
7	0.0512	0.0494	1.04	0.0978	
8	0.0488	0.0484	0.97	0.1321	
11	0.0455	0.0475	0.97	0.1183	
12	0.0641	0.0592	1.08	0.1460	
13	0.0212	0.0305	0.69	0.1175	
15	0.0517	0.0494	1.05	0.1044	
16	0.0401	0.0447	0.89	0.1091	
17	0.0409	0.0457	0.89	0.1171	
25	0.0512	0.0493	1.04	0.1120	
26	0.0426	0.0461	0.92	0.0860	
4	0.1199	0.0895	1.34	0.1670	NORMAL
9	0.0865	0.0714	1.21	0.1516	
20	0.1926	0.0980	1.94	0.1682	
21	0.0875	0.0734	1.19	0.1740	
22	0.1533	0.0949	1.57	0.1797	
24	0.0924	0.0804	1.15	0.1683	
6	0.2000	0.1016	1.96	0.2006	GOOD
10	0.2529	0.1378	1.83	0.2177	
18	0.4006	0.2026	1.97	0.2559	
19	0.2815	0.1435	1.96	0.2321	
23	0.2411	0.1353	1.79	0.1824	

It has further been observed from the analysis of Sagar soils and their comparative study with regur soils that the former can be broadly classified among the Black Cotton soils of the Southern Plateau with respect to their various physical and chemical characters, as detailed in the table No. 3. Various other features, such as cracking, high yield potential etc. on the systematic treatment and care, are also common to both.

TABLE No. 3

	Regur Soils	Sagar Soils	Remarks
1—Colour	Black with slight variations due to mixing of red & black soils in varying proportions.	Similar variations in colour.	
2—pH	7.2—8.5	7.1—8.9	
3—CaO	0.28—4.48% (exceptionally, 0.056—11.20%)	1.1281—4.1004% (exceptionally, 3.4892—22.2% in chalky soils.)	
4—Organic carbon.	0.03—0.8%	0.1468—1.855%	Total carbon expressed in Sagar Soils.
5—Nitrogen	0.04—0.06%	0.0305—0.2026%	
6—Clay	40—60%	32.46—51.37%	13.36% in chalky soil as exception.
7—Cation exchange capacity.	40—60 m. e. per 100 gs of soil	42.76—56.85 m. e. per 100 gs of soil	

Thus, a careful and systematic analysis of Sagar soils lead to the conclusion that :—

(1) They can be grouped into three distinct classes as “inferior, normal and good” with respect to their phosphorus and nitrogen content.

(2) The nitrogen status of soils depend upon their phosphorus status, i.e., soils rich in  $P_2O_5$  content are rich in nitrogen status and vice-versa.

(3) They can be broadly classed among the Regur or the Black Cotton Soils of the Southern Plateau.

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# ORGANIC PHOSPHORUS CONTENT AS AN INDEX OF FERTILITY OF SOME INDIAN SOILS

By

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(Received on 23rd December 1955)

Fertility of a soil is a term which normally refers to the available nutrient status. The three major nutrients generally control the fertility of a particular soil. All Indian soils contain sufficient amount of potash but are generally deficient in nitrogen and phosphorus. The agricultural practices like green manuring and addition of organic and inorganic manures to soils puts nitrogen to a much better position. Phosphorus nutrition, however, presents difficulty. The calcareous soils present even a greater difficulty when pure inorganics are applied. There use of bulky organic manures and super-phosphate is suggested (3). The importance of organic phosphorus compounds in soils has been much stressed by a number of workers as they are more available to plants (1, 5, 11). Its importance in the tropical countries has been all the more stressed. Eid et al making use of mis-terlich's pottest technique has definitely shown that availability of organic phosphorus is a factor effective in tropical soils (5).

Patel and Vishwanath made a comparative study of Indian soils with regard to phosphate fixation capacity (12). They found that Black cotton soils of C. P. & Berar, Bombay and Deccan have the highest fixation capacity. It appears on the contrary that these black cotton soils with very high fixation capacity have availability of phosphorus to crops as the crops generally do not show phosphorus deficiency. The Black soils of Berar and few Karail soils of U. P. and Bihar which are essentially calcareous in nature exhibit excellent productivity (7). However, Black cotton soils of lighter texture as are found in certain parts of Yeotmal, Buldana, Dhar, Dewas, Ujjain and Satna districts and other parts of India are less productive. These soils in contrast to rich black cotton soils show some significant response to phosphates in leguminous crops which require more of phosphates for their growth, but not in cereals which require comparatively much less phosphorus for their growth (2).

It has been reported that organic phosphorus compounds are retained by soil clay and that the adsorption is dependent upon a number of factors. The retention has been shown to be directly proportional to the amount of clay minerals present (1, 6). It, therefore, seems not improbable that difference in clay content and its composition may result in the variation of organic phosphorus status of a soil. It may be concluded in the light of above observations that organic phosphorus may be one of the important factors in determining the fertility status of Indian soils as against nitrogen which presents little difficulty in inorganic and organic manuring.

In the present investigation, a study of the organic phosphorus status and the fertility status of different soils is made.

## METHODS AND MATERIALS

Various soil profiles obtained from different parts of India were analysed for organic carbon, and organic phosphorus. Organic carbon was determined by carbon

combustion furnace method of A. O. A. C. and Organic Phosphorus by Pearson's technique (4, 8). Comparison of colour was done on Gallen Kamps photoelectric colorimeter.

#### RESULTS

The results in Table No. 1 and 2 indicate that there is a definite difference between the organic phosphorus content of the light textured and heavy textured soils :—

TABLE No. 1

Organic Carbon and organic phosphorus content of soils having low clay per centage.

Locality	Depth Inches	Organic P p.p.m.	Organic C %	Orgc./ Org. P.
Banaras ...	0 - 6	41.0	0.492	123.0
	6 - 12	43.0	0.596	138.6
	12 - 18	26.0	0.498	191.5
Kodai ...	0 - 6	45.0	0.390	86.6
	6 - 17	36.0	0.320	88.8
Satna (Red) ...	0 - 6	27.0	0.530	196.3
	6 - 12	31.0	0.510	164.5
	12 - 24	28.0	0.322	115.0
Nathikhera ... (Red)	0 - 9	23.0	0.940	408.0
	9 - 30	15.3	0.344	224.8

The soils with lighter texture show organic phosphorus content as low as 15.3 p.p.m. and in no case above 45 p.p.m. The organic phosphorus content is more in soils of Indogangetic planes *viz.* Banaras and Kodai; whereas Red soils of Satna and Nathikhera show least organic phosphorus status.

TABSE No. 2

Organic phosphorus and organic carbon content of soils having a high clay percentage.

Locality	Depth Inches	Organic P p.p.m.	Organic C %	Orgc./Org. P
Shahanshapur (Karail) ...	0 - 6	65.0	0.160	24.6
	6 - 12	163.0	0.456	26.8
	12 - 18	113.0	0.412	36.4
Nagpur Black ...	0 - 18	88.0	0.392	46.6
	18 - 39	23.0	0.436	189.5
Satna Dark Black (Mair)...	0 - 6	83.0	0.491	59.1
	6 - 12	88.0	0.412	47.8
	12 - 24	80.0	0.410	50.1
Satna (light black) ...	0 - 6	49.0	0.430	87.7
	6 - 12	41.0	0.270	65.8
	12 - 24	43.0	0.180	41.8

The soils with heavier texture show a minimum of 23 p.p.m. at a depth of 39" but that maximum is as high as 163 p.p.m. in Shahanshahpur soil. Soils with heavier texture in general have a higher organic P. status. Light Black soil of Satna has a lower organic P status i.e. 49 - 41 p.p.m.

The table No. 3 shows the yields of major crops in different soils. Satna Red and Nathikhera Red soils give very low yields for all crops. The Satna light and black, Banaras, Kodai and Nagpur soils give normal yields ranging from 880 - 640 lbs per acre for wheat, 720 - 640 lbs per acre for gram and 600 lbs per acre for juar. Shahanshahpur (Karail) and Satna (Mair) are very productive soils. The yields are 1600 - 960 lbs per acre for wheat, 1800 - 1040 lbs per acre for gram. The juar yields are very good for Satna Mair soil, i.e. 1200 lbs per acre even at a low seed rate.

TABLE No. 3  
Average yields of important crops in different soils under unirrigated conditions.

Locality	Description	Rainfall (Inches)	Wheat lbs per acre	Gram lbs per acre	Juar lbs per acre
Banaras	... Alluvial	40 to 50	880	720	-
Kodai	... Do	Do	Do	Do	-
Satna Red	... Light soil	30 to 35	480	480	480
Nathi Khera	... Do	20 to 30	400	400	480
Shahanshahpur (Karail)	... Very heavy Deep black	40 to 50	1600	1800	-
Nagpur	... Heavy black soil.	Do	640	640	600
Satna (Mair)	... Very heavy Deep black	30 to 35	1040	1120	1200
Satna (Black)	... Heavy Black soil.	Do	720	640	600
All India Average...			723	364	496

The Shahanshahpur Black Karail and Satna (Mair) resemble very much in various characteristics. The difference in the yield of the two can be accounted for due to difference in rainfall.

Maximum rainfall is observed in Banaras, Kodai, Shahanshahpur, Nagpur soils, i.e. 40" to 50". The areas of Satna and Nathi Khera are comparatively drier having a rainfall ranging from 20" to 35". Except for soils of Kodai, Banaras and Shahanshahpur dry farming is the usual practice for raising the crops due to only one rainy season, i.e. from July to September. The Banaras, Kodai and Shahanshahpur soils have 2 rainy seasons—one from July to September and the other in January. The lower yields in certain black soils as compared to soils of Indogangetic plains is due to no rains in January, which brings in inevitably an



earlier harvesting season and consequently a lower yield. A well marked effect of rains during the January season is observed in the entire black soil region. Table No. 4 gives yields of juar and groundnut at the Akola Farm for two years. In 1952-53, the rainfall was 22.03" all during July to September. In 1953-54 there was a total rainfall of 25.38", but spread over the year. The results clearly show that yields of juar were increased 3 times and groundnut more than 2 times.

TABLE No. 4

Yields of juar and groundnut on Government Farm, Akola.

Year	Rainfall	Yields of juar lbs. per acre	Yields of groundnut lbs. per acre
1952-53	22.03	540	527
1953-54	25.38	1,597	1,103

Results of the mechanical analysis of some very fertile, medium and poor soils are presented in table No. 5.

TABLE No. 5

Mechanical analysis of surface layers of some typical soils

Locality	Clay %	Silt %	Fine Sand %	Coarse Sand %	Fertility status
Karail soil (Bheri) ..	59.4	18.38	8.85	0.29	Very fertile.
Black cotton soil, Nagpur.	40.0	33.00	7.40	0.05	Fertile.
Yellow soil (Sehar, Nagpur).	24.55	25.00	34.55	9.77	Medium.
Red Soil (Bhata) ...	14.93	14.40	17.67	51.76	Poor.

Results indicate that soils with higher clay percentage as are black soils have a higher fertility status whereas soils of red and yellow colour have low and medium fertility status and have definitely lower clay percentage.

#### DISCUSSION

Studies of organic phosphorus status of various soils indicate that heavier texture is usually associated with higher organic phosphorus content and *vice versa*. The association of soils with a heavier texture with high organic phosphorus content provides circumstantial evidence as to the part of clay content in retaining organic phosphates. Goring, Barthelomew and Bower (1,6) have definitely shown that organic phosphates can be retained by clay minerals present in the soil. The

analysis (Table Nos. 1,2,5) also reveals that deep black soils with highest clay percentage contain maximum organic phosphates. The alluvial soils with lower clay percentage contain lesser organic phosphates, whereas the red soils with least clay percentage contain least organic phosphates. It is very important to note in this connection the nature and composition of clay minerals which may lead to various variations. It may be pointed out here that in all the black soils under study showing high fertility and organic phosphorus content montmorillonite is the predominant clay mineral. The clay content is usually much higher than the corresponding red or light coloured soils (9).

The lighter soils generally give lower yields as compared to soils with heavier texture and this is well marked in black soils. The black soils with very deep black colour containing 60—70% clay are supposed to be most fertile soils. The Karail soils of U. P. and Bihar (7), Mair soils of Vindhya Pradesh and deep black cotton soils of Berar, Deccan and Bombay are extremely productive. In table No. 3 we find that Karail and Mair soils of Shahanshahpur and Satana respectively are very productive. The black soils of light texture as found in Satna and Nagpur are not so fertile and productive. The yellow alluvial soils of indogangetic planes and black soils of Satna and Nagpur give medium yields. Black soils mentioned here have 40—45% clay. Rainfall is an important consideration in these black soils as their power of retaining water is also low, and therefore, a rainfall during January has a well marked effect. A higher rainfall normally results in better yields as is evident from the results presented in Table No. 4. These soils, therefore, appear to be inherently more fertile than the soils of Indogangetic alluvium which get sufficient rainfall spread over the year. However these black soils are less productive than the soils of deep black colour from whom they differ in being lighter textured and containing lesser organic phosphates. Total carbon is nearly equal (Table No. 2). The red soils are generally very loose and much leached soils. These are poor soils. The results in Table No. 3 indicate that of all the soils studied, the red soils are the poorest. The organic phosphorus and clay content also is least in these soils.

The association of most fertile soils with a high clay percentage and a high organic phosphorus content easily leads one to conclude that higher clay percentage has resulted in the retention of more of organic phosphates which accounts for the rich productivity. Indian soils in particular have a high assimilation and mineralisation rate (10). It is highly probable that during the periods of decomposition of organic matter the assimilated organic phosphates are retained by clay minerals present in soil and are later utilised by crop. The medium and poor soils reveal a lower organic phosphorus status which leads to lesser productivity. The lesser organic P status in these soils is probably due to the low clay percentage that they contain.

All Indian soils contain sufficient amount of potash and nitrogen manuring is also done in an effective manner. Thus a supply of available nitrogen is maintained in soils. The phosphorus nutrition on the other hand is not so effective as the mineralisation and assimilation are very quick. If somehow the organic phosphates are retained better returns are obtained. Thus organic phosphates become an important factor in determining fertility status. As the organic phosphorus content of soils contributes largely to the available phosphorus status in tropical soils it should be possible to judge the fertility status of soils by knowing the organic phosphorus content. On the basis of evidences obtained above it seems possible to assess the fertility of tropical soils in general by estimating its organic phosphorus content,

### SUMMARY

Analysis of deep black, light black, yellow alluvial, and red soils from different parts of India is made for organic phosphorus and organic carbon. Results indicate that black soils with highest clay percentage contain maximum organic phosphorus content and the soils with lighter texture lesser organic phosphates. Clay percentage is found to be in the following order :—

Deep Black > Light Black > Yellow alluvial > Red soil.

It is suggested that retention of organic phosphates is effected by clay minerals. Fertility of the soils is also in the above order which suggests that soils with higher organic phosphorus status are more fertile and *vice versa*. Authors have suggested that organic phosphorus content may be successfully employed as an index to fertility of Indian soils.

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# STUDIES OF NUTRIENT DEFICIENCY AND THEIR INTER-RELATIONSHIPS IN PLANT GROWTH MAIZE CROP

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## INTRODUCTION

The mineral theory of nutrition of crops enunciated by Liebig as early as 1840 was the starting point to investigate the mineral needs of plants. This led to the important study of optimum conditions, concentration and balance among nutrient elements when limiting factors of sufficiency or deficiency of mineral nutrients cropped up. Little progress was made till recently when on the one hand the field experiments at Rothamstead were conducted to bring out the effect of mineral nutrients on crops and on the other agricultural chemists concentrated their attention on soil analysis as a method of determining mineral deficiencies. Chemicals examination of soil has not satisfactorily solved the problem of plant nutrition—the problem, not being simple since while soils contain a considerable amount of a given nutrient the plants in such soils have suffered from the deficiency of the same element. For, the paradox, as it would seem, raised the question of their availability to crops of various elements in different soils. Then, of course, various methods were adopted by groat workers like Neubauer-rye seedlings to extract  $K_2O$  and  $P_2O_5$ —and also other biological methods, within the past three decades great advances have been made after the standardisation of the methods of plant analysis. At the initial stage even this dependable method of plant analysis to ascertain the mineral requirements was not without defects as in the case met by Lawes who contradicted the conclusion of Liebig on phosphate requirements of turnips since then, methods were modified to determine mineral deficiencies of crop plants. Ulrich's work on phosphate content and yield of Ladino clover has been more then convincing as to how, of the various organs of the plant, the leaf analysis may be used for the diagnosis of nutritional deficiency and it is obviously so since the leaf is the seat of active growth processes. With this as the background an attempt was made to study how far plant analysis particularly analysis of the leaf will reflect the true picture of the nutritional status.

## MATERIAL AND METHODS

The maize crop in the N. P. M. field, central Farm, Coimbatore, which has been receiving exclusively different fertilizers for the past 20 years, was utilised for this study. The following were the treatments. No manure, N, P, N, NP, NK, PK, NPK, cattle manure and cattle manure residual. In other words, in addition

to no manure, complete manure and cattle manure, there were single deficiency treatments namely NK, NP & PK, and compound (double) deficiency treatments namely N, P and K. There are two series, the Eastern Series and the Western Series and the Western Series has been receiving a basal dressing of cattle manure. Observations for deficiency symptoms; plant characteristics were made and samples were taken at the five important physiological stages of growth, namely seedling, vegetative, flowering, milk and harvest stages. The samples of leaf, stem and root were analysed for N,  $P_2O_5$ ,  $K_2O$ , lime and magnesia. The pH of the sap of various parts of the plant at various stages of growth was also recorded. The data of chemical analysis of the leaf, etc., and other data are given in tables.

#### OBSERVATIONS

*Eastern Series*—It may be observed that:

(1) In the case of nitrogen, the fall in nitrogen content in the leaves is slow in the absence of N, but in the absence of P and K by the application of N, the fall in nitrogen content is more steeper, as a contrast with NPK.

(2) The fall in  $P_2O_5$  content of leaves has been gradual from seedling to flowering stages, and there after less steep up to the harvest stage in the case of no manure, NK, and N treatments. NPK also behaves in the same way except that the  $P_2O_5$  content is more obviously; whereas in the case of P, PK and K treatments there is a considerable rise of  $P_2O_5$  during the vegetative stage and then a steeper fall to the flowering stage and there after behaving more or less on similar lines as other treatments.

(3) The fall in the Potash content of the leaves is smooth in the case of no manure, NP and NPK, except that NPK, has got a higher Potash level. In the case of K and NK, the Potash content appears to have a low fall up to vegetative stage and then a very steep one to the very end of harvest stage, both the cases, being phosphorus deficient.

(4) In the case of leaves at any stage, the variation in the nitrogen content is more pronounced in single deficiency group than double deficiency group. Similar trends are observed in  $P_2O_5$  and  $K_2O$  also.

(5) In general, the variations in the nutrient contents of roots between single and double deficiency treatments are not pronounced. In the case of stems, however, unlike the leaves, there is a contradictory nutrient balance between the single and double deficiency treatments, from vegetative to flowering stages. Besides, the nutrient contents are not faithful reflections of the treatments at either stage.

(6) While NPK treatment gives the highest yield, the deficiency of K or N or both has not so adversely affected the yield as deficiency of P itself. As a corollary, application of N in the absence of P, with or without Potash deficiency has not been effective to increase the yield.

(7) Practically there is not much of variation in pH of the sap of leaf, except that there is a slight tendency of a fall in pH at the harvest stage, compared against the seedling stage. In the case of stem there is a slight increase. In the case of root, there is more constancy of the pH level.

*Western Series*—In general the data are not in line with the Eastern series though  $P_2O_5$  ingredient bears a somewhat similar relationship at various stages

and among treatments. The Western series differs from the Eastern Series in that the former has received a basal dressing of cattle manure.

#### DISCUSSION

The fall in nitrogen content in the leaves has been uniformly steep in no manure as well as N deficient treatments. Nitrogen alone has had the same steep fall when contrasted with NPK. Thus addition of P and K has altered the gradient. The control of nitrogen fall in the leaf in the presence of P & K, seems to have influenced the increase in yield. This again clarifies that nitrogen application alone has failed to increase the yield, when P and K are deficient.

The phosphorous relationship is more related not only with the nutrient balance but the yield as well. It is natural that no manure, N, NK show a poor  $P_2O_5$  content and N, P, K, higher level of  $P_2O_5$ . The interesting fact to be considered is how in the absence of N i.e. P, PK and K treatments, there is a considerable rise of  $P_2O_5$  in the leaves during the vegetative stage. How far the presence of P can make good the absence of N is not quite well known. P like N is closely concerned with the essential growth processes in plants, in the formation of nucleic acid, the essential part of all living cells. In the metabolism of fats and in the process of respiration, with the utilization of N, P functions most effectively. Thus even though N is deficient with the available N as from no manure, P probably replaces N in the vegetative stage.

In a somewhat similar trend is the conservation of K when P or P and N are deficient when considering the  $K_2O$  contents of leaves. The high mobility of potassium within the plant when the element is in short supply can very well explain the possible conservation when P and N are also absent.

Then again for the observation that differences in nutrient intake being more pronounced in single deficiency treatments than double deficiency treatments, it is possible that when the two of three important major nutrients are present in just adequate amounts, it is unlikely to effect greater intake. The deficiency of one element may effect the intake of another, and as a corollary it need not follow that the presence of one or two major nutrients in adequate amounts must effect the greater intake when there is a deficiency. It is probable, for example, P can replace the functions of N to a limited extent, when K is there. When K is also absent, the function of K also has to be substituted. In such a situation, it might be possible that changes may take place inducing some intake of either of them or both of the nutrient elements. This may explain away the pronounced difference in nutrient content in single deficiency treatments against double deficiency treatments.

From the observations that such differences small as they themselves are, are not noticeable in stems in general and roots in particular. It can be said that leaf analysis may be more dependable than other organs of the plant. In the Wadino clover experiments of which, it was noted that P content of leaf tissue increased up to a critical level, to which yield was correlated, whereas low concentration of P on the contrary was associated with decreased yield. The leaf being the seat of all growth processes, it faithfully reflects the nutritional status of the soil. Maximum nutrients are assimilated by the plant at full vegetative stage of growth.

The variation in the analytical data as well as the yield data of the Western Series, can be ascribed to the application of a basal dressing of cattle manure, which probably annuls the effect of ideal deficiencies.

#### CONCLUSION

- (1) The analysis of leaf is a true index of nutritional status.
- (2) P better than N or K can replace the functions of the missing elements effectively to some extent when there is a single deficiency rather than double deficiency.
- (3) Lowering of yield is more pronounced in the absence of P rather than in that of N or K.

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# EFFECT OF PHOSPHATES ON NITROGEN LOSS

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When artificial nitrogeous fertilizers like ammonium sulphate or urea are added to the soil<sup>1-3</sup>, a major portion of their nitrogen content is not utilized by plants and a good deal of it is lost as nitrogen gas. It has reported by Lohnis and Fred,<sup>3</sup> that of the important three plant nutrients—nitrogen, phosphorus and potassium—the recovery of nitrogen is lowest, about 40—50%, whereas the recovery of potassium and phosphate may be as high as 70—80%. The aim of this work is to study the effect of different phosphates in combination with the organic substance sawdust on the loss of nitrogen suffered when ammonium sulphate or urea is added to the soil.

## EXPERIMENTAL PROCEEDURE

200 grams of well powdered soil after having been passed through a 80 mesh sieve per inch were taken in 250 c.c. beakers, 0.5% carbon in the form of powdered sawdust was added to this soil, 0.1% nitrogen either as ammonium sulphate or urea was added to these mixtures. In some beakers 0.2%  $P_2O_5$  as dicalcium phosphate or tricalcium phosphate was also added. These beakers were placed under a 500 watt electric bulb hung over the table at a distance of  $2\frac{1}{2}$  feet. The exposure was carried on for a period of four months, eight hours per day. A similar set of beakers containing the same amounts of materials were placed besides these beakers covered with a thick black cloth. The moisture of the system was maintained at 20%. The contents of the beakers were stirred on every alternate day with a glass rod. Total carbon and total nitrogen of the exposed material, were determined first after a period of two months and then after another two months.

Carbon present in the samples of soils was estimated by the method described by Robinson, McLean and Williams<sup>4</sup>. The total nitrogen was determined by the Kjeldahl salicylic acid reduction method. All the soil samples more oven dried before analysis.

Following is the composition of the soil used in this work.

CaO=4.31%      Total carbon=1.7453%

MgO=1.71%      Total nitrogen=0.2373%

$K_2O$ =1.14%

$P_2O_5$ =0.413%

Temperature of the system exposed to electric bulb or kept in the dark 30°.



EXPERIMENTS WITH AMMONIUM SULPHATE  
200 grams soil + 0.1% N as Ammonium Sulphate.

Period of exposure in days	Total carbon %	Total nitrogen %	Nitrogen Loss %
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Exposed

0	1.7453	0.3373	—
60	1.7419	0.2757	61.6
120	1.7401	0.2688	68.5

Covered

0	1.7453	0.3373	—
60	1.7448	0.2930	44.3
120	1.7436	0.2831	54.2

200 grams soil + 0.1% N as Ammonium Sulphate + 0.5% C as Sawdust

Exposed

0	2.2241	0.3439	—
60	2.0357	0.2995	44.4
120	1.9606	0.2917	52.2

Covered

0	2.2241	0.3439	—
60	2.1087	0.3132	30.7
120	2.0703	0.3052	38.7

200 grams soil + 0.1% N as Ammonium Sulphate + 0.5% C + 0.2%  $P_2O_5$   
as Tricalcium phosphate

Exposed

0	2.2234	0.3440	—
60	2.0181	0.3086	35.4
120	1.9867	0.2997	44.3

Covered

0	2.2239	0.3437	—
60	2.1155	0.3234	20.3
120	2.0682	0.3130	30.7

200 grams soil + 0.1% N as Ammonium Sulphate + 0.5% C + 0.2%  $P_2O_5$  as  
Dicalcium Phosphate

Period of exposure in days	Total Carbon %	Total nitrogen %	Nitrogen Loss %
Exposed			
0	2.2234	0.3442	—
60	2.0166	0.3111	33.1
120	1.9403	0.3025	41.7
Covered			
0	2.2241	0.3439	—
60	2.0942	0.3253	18.6
120	1.9328	0.3158	28.3

EXPERIMENTS WITH UREA

200 grams soil + Exposed 0.1% N as Urea

0	1.7449	0.3373	—
60	1.7429	6.2668	70.5
120	1.7415	0.2594	77.9

Covered

0	1.7449	0.3373	—
60	1.7440	0.2858	51.5
120	1.7429	0.2777	59.6

200 grams soil + 0.1% N as Urea + 0.5% C as Sawdust

Exposed

0	2.2240	0.3439	—
60	2.0353	0.2915	52.4
120	1.9602	0.2836	60.3

Covered

0	2.2241	0.3439	—
60	2.1082	0.3177	26.2
120	2.0701	0.3105	33.4

200 grams soil + 0.1% N as Urea + 0.5% C + 0.2%  $P_2O_5$  as Tricalcium Phosphate

Period of exposure in days	Total carbon %	Total nitrogen %	Nitrogen loss %
Exposed			
0	2.2230	0.3435	—
60	2.1328	0.2977	45.8
120	1.9972	0.2916	51.9
Covered			
0	2.2236	0.3435	—
60	2.1531	0.3211	22.4
120	2.0599	0.3156	27.9

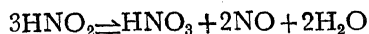
200 grams soil + 0.1% N as Urea + 0.5% C + 0.2%  $P_2O_5$  as Dicalcium Phosphate

Exposed			
0	2.2236	0.3439	—
60	2.0170	0.3006	43.3
120	1.9408	0.2933	50.6
Covered			
0	2.2241	0.3439	—
60	2.0938	0.3247	19.2
120	1.9325	0.3177	26.2

#### DISCUSSION

A careful study of the foregoing experimental results clearly indicates that when artificial nitrogenous fertilizers like ammonium sulphate or urea are added to the soil, there is a considerable loss of nitrogen. Urea suffers greater loss than ammonium sulphate. The loss of nitrogen is invariably higher in the exposed sets as compared with the covered ones. The rate of loss is rapid in the beginning but slows down with the passage of time.

Dhar<sup>5</sup> has offered a satisfactory explanation of these heavy losses of nitrogen. In the process of nitrification taking place in the soil an unstable compound ammonium nitrite is formed which decomposes into nitrogen gas and water and thus causes the loss of nitrogen. The formation of ammonium nitrite from ammonium salts or proteins requires oxygen and that is the reason why this type of denitrification is helped by soil aeration and soil acidity as nitrous acid also undergoes decomposition according to the equation



This chemical change is also markedly accelerated by light.

These results also indicate that on the incorporation of the organic matter i.e., sawdust with these fertilizers, the loss of nitrogen is markedly checked. These observations show that the energy rich materials like sawdust which is rich in carbon has got a retarding effect on the decomposition of nitrogenous compounds. It has also been observed that the energy rich substance gradually undergoes oxidation and the carbon content of the system decreases. The retarding influence of these materials of organic origin can be explained on the basis of negative catalysis. It seems that these materials which are carbonaceous act as negative catalysts and thus check the oxidation of nitrogenous compounds. It is known that the carbohydrates preserve body proteins from undergoing oxidation and it is just likely that the carbonaceous matter present in the soil may also be able to protect the soil protein and the nitrogenous material from oxidation.

These results further indicate that when dicalcium and tricalcium phosphates are added along with the organic matter and the artificial fertilizer, the loss of nitrogen is still more checked. Dicalcium phosphate has a better effect than the tricalcium.

The retarding effect of these phosphates may be explained on the view that they form stabler calcium nitrite from ammonium nitrite and calcium ion obtainable from calcium phosphates with the consequence that there is a decrease in the loss of nitrogen. Moreover the phosphates markedly enhance the efficiency of nitrogen fixation when added to the soil along with the organic matter which goes a long way in neutralising the loss. In nitrogen fixation<sup>6</sup> experiments it was observed that the dicalcium phosphate enhances the efficiency more than the tricalcium phosphate, hence greater check of loss of nitrogen with the di than the tricalcium phosphate.

Besides it is probable that the phosphates may form some stabler kinds of phospho proteins which are more resistant to oxidation than the ordinary proteins. This may also be one of the factors contributing to the check of the loss of nitrogen. Thus it may be said in the end that phosphates seem to play a vital role in checking the nitrogen loss.

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# NITRATE FORMATION AND FIXATION OF ATMOSPHERIC NITROGEN IN ALKALI AND NORMAL SOILS ON THE ADDITION OF ORGANIC SUBSTANCES CONTAINING SMALL AMOUNTS OF PHOSPHATES

By

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In his Presidential Address to the National Academy of Sciences, India, 1952, Dhar<sup>1</sup> has stated as follows:—

“It will be interesting to record here that the average temperature of Allahabad is 26° whilst that of Rothamsted is about 8° and at Uppsala 5°. The total nitrogen content of average Rothamsted soil is 0.12% against 0.04 in Allahabad. It is clear, therefore, that the organic matter added to the soil at Allahabad is oxidised at a speed three times greater than that at Rothamsted, i.e., for an increase of 18°, the velocity of oxidation of carbonaceous substances becomes three times greater.

It is well known that the temperature co-efficient of the chemical reactions for a 10° rise in temperature taking place in the homogeneous medium can vary from 2 to 7, whilst reactions taking place in a heterogeneous system usually show a temperature co-efficient about 1.2 or 1.3 and much less than 2 for a 10° rise. Hence it appears that oxidation of the organic substances in soil and the formation of humus takes place in a heterogenous phase and not in homogenous conditions. Jenny has reported that a fall of 10° in mean temperature doubles or trebles the nitrogen content of the soil i.e., the relationship is almost exponential. It appears that Jenny has reported a more marked influence of temperature as in homogeneous reactions, but it appears to us that the soil oxidation reactions by which the humus content, availability of nitrogen, pH values and carbon/nitrogen ratio and loss of nitrogen etc. are controlled, take place in the heterogeneous phase on the soil surface.”

Moreover from our experimental results recorded in the following pages it will be seen that the carbon/nitrogen ratio of alkali soil is much smaller than 10, frequently this ratio in the alkali soils of India may be as low as 3. In other words the percentage of nitrogen present in the humus of the soil depends on its pH value. The greater the pH, the greater is the percentage of nitrogen present in the humus of the soil.

It is well known that in cold countries leaching of the soil by rain removes calcium but as the cold country soils are richer in humus and carbonic acid than hot country soils the calcium in cold country soils is not replaced so much by Na-ions but is usually replaced by H-ions. Hence the formation of alkali soils seems to be easier in hot countries than cold countries. It is well known that the soil humus acts as a marked adsorbent of ions and as buffer; hence soils rich in humus are not likely to be too acidic or too alkaline. It is well known that in hot countries the

soil organic matter incorporated and soil humus undergo quick oxidation which is always facilitated by alkalinity. It has been repeatedly observed that acid retards oxidation processes by air and alkalinity accelerates them. Hence when a soil becomes alkaline and if organic matter is not added to such soil the percentage of alkalinity is likely to go on increasing, chiefly due to a loss of humus by oxidation. This process seems to be autocatalytic as alkalinity increases in course of time. The net effect is that in hot countries the alkali soils become extremely poor in humus. This is clear from the table given below :—

Analysis of the alkaline soils from different places.

Places			Total Carbon	Total Nitrogen	C/N Ratio	pH
			%	%		
1.	Soraon (Alld. Distt.)	...	0.1143	0.0334	3.42	10.7
2.	" "	...	0.1160	0.0350	3.31	10.3
3.	Faizabad (U. P.)	...	0.2220	0.0750	2.99	9.8
4.	" "	...	0.2370	0.0400	5.93	9.7
5.	" "	...	0.5400	0.0823	5.35	8.6
6.	" "	...	0.2400	0.0621	3.85	9.4

In the following pages, we have reported our experiments on the formation of nitrates by mixing different organic substances with normal and alkali soils. It is well known that the production of nitrates in soil is essentially an oxidation reaction.

It is generally believed that in cold countries if the total nitrogen content of the organic material added to soils is less than 1.8% the mineral nitrogen content present in the soil decreases but with materials richer in nitrogen the available nitrogen increases on the decomposition of the organic substances added. This is clear from the following results obtained by S. A. Waksman and F. G. Tenney<sup>2</sup>.

Relation between the nitrogen content of various plant roots and the nitrate-nitrogen in the soil.

Material used	Nitrogen content of the material	Weight of the material added	Nitrate-nitrogen in the leaching	Gain or loss of nitrogen
	%	gms.	m.gms.	m.gms.
1. Control soil ...	...	...	947	---
2. Oat roots ...	0.45	133	207	- 740
3. Timothy roots...	0.62	97	398	- 549
4. Maize roots ...	0.79	76	511	- 436
5. Clover roots ...	1.71	35	925	- 22
6. Dried blood ...	10.71	5.6	1750	+ 803

They used powdered plant roots and dried blood and incubated these materials with soil and after three months, the soils were leached and the nitrate content determined. From their results it is clear that ground clover roots containing 1.7% total nitrogen causes only a slight decrease in nitrate nitrogen of the soil, whilst with other materials rich in carbon and possessing the carbon/nitrogen ratio greater than 10, the decrease of nitrates were more pronounced but with dried blood having the carbon/nitrogen ratio much less than 10, there was marked increase in nitrate nitrogen in the soil after three months. H. L. Jensen<sup>2</sup> also reported that the rotting of nitrogen poor plants or animal remains in a soil will lower its content of mineral nitrogen i.e., ammonium and nitrate ions, whilst the rotting of a nitrogen rich material will increase it.

We have repeated experiments of this type carefully both with alkaline and normal soils using lignite, wheat straw, clover, Koodju (*Pueraria thunbergiana*), cow-dung and oil-cake (at the rate of 600 m.gms. of nitrogen to 28 lbs. of soil) and have determined the total nitrogen, total carbon and nitrate nitrogen after six months exposure to electric bulb (100 Watt) light. Analysis of the materials used are given below :—

Analysis of the materials used.

Material used	Total carbon %	Total nitrogen %	Carbon/ nitrogen Ratio
Alkaline soil	0.1143	0.0334	3.42
Normal soil	0.5080	0.0628	8.09
Lignite	60.0001	0.5600	107.15
Wheat straw	40.0000	1.0410	38.43
Clover	38.0198	1.7200	22.11
Koodju ( <i>Pueraria thunbergiana</i> ).	35.0140	1.8000	20.01
Cow-dung	9.8000	0.4500	20.18
Oil cake	35.4500	4.5000	7.88

#### EXPERIMENTAL PROCEDURE

500 grams of well dried and powdered (sieved through 1 mm. sieve) soils (both alkaline and normal) was taken in shallow enamelled dishes and 23.6205 m.gms. of nitrogen (i.e., at the rate of 600 m.gms. to 28 lbs. of soil) contained in lignite, wheat straw, clover, koodju (*Pueraria thunbergiana*), cow-dung and oil-cake was added. The materials were well dried and powdered in agate pestle-mortar and passed through half m.m. sieve before adding to the dishes.

The ingredients were mixed thoroughly and samples were taken out for the initial reading. Distilled water was added daily to bring the moisture content to about 20%. The soil mixtures were stirred almost daily. An exposure of 6 months

under an electric bulb (100 Watt) placed at a distance of 1 yard from the dishes, was given. The average temperature attained by the mixture was 32°. After 6 months exposure the samples were taken out and analysed for total carbon, total nitrogen and nitrate-nitrogen according to the standard methods.

A control soil was also kept side by side of the other dishes. Results calculated on oven dry basis are recorded in the tables 1 to 8.

(a) *Normal soil*

Mean temperature during exposure—32°

Date of starting the experiment 2—2—52.

TABLE 1  
*Nitrate nitrogen*

Material used		Nitrogen content of the material added.	Weight of material added in 500 gms. soil.	Nitrate nitrogen in the leachings	Gain or loss of nitrogen (nitrate)
		%	gms.	m.gms.	m.gms.
1. Control soil	...	0.0628	...	20.8	...
2. Lignite	...	0.5600	4.2180	23.2	2.4
3. Wheat straw	...	1.0410	2.2690	25.1	4.3
4. Clover	...	1.7200	1.3733	26.6	5.8
5. Koodju ( <i>Pueraria thunbergiana</i> )	...	1.8000	1.3133	26.5	5.7
6. Cow-dung	...	0.4500	5.2419	29.4	8.6
7. Oil cake	...	4.5000	0.5242	29.8	9.0

TABLE 2  
*Total nitrogen*

Material used		Nitrogen content of the material used.	Weight of the material added in 500 gms. soil.	Total nitrogen before exposure	Total nitrogen after exposure
		%	gms.	%	%
1. Control soil	...	0.0628	...	0.0628	0.0628
2. Lignite	...	0.5600	4.2180	0.0670	0.0673
3. Wheat straw	...	1.0410	2.2690	0.0670	0.0680
4. Clover	...	1.7200	1.3733	0.0670	0.0682
5. Koodju ( <i>Pueraria thunbergiana</i> )	...	1.8000	1.3133	0.0670	0.0679
6. Cow-dung	...	0.4500	5.2419	0.0670	0.0732
7. Oil cake	...	4.5000	0.5242	0.0670	0.0692



TABLE 3

*Total carbon*

Material used	Carbon content of material	Weight of the material added in 500 gms. of soil.	Total carbon before exposure.	Total carbon after exposure.
	%	gms.	%	%
1. Control soil ...	0.5080	...	0.5080	0.5040
2. Lignite ...	60.0001	4.2180	1.0142	0.9742
3. Wheat straw ...	40.0000	2.2690	0.6895	0.6101
4. Clover ...	38.0198	1.3733	0.6125	0.5527
5. Koodju ( <i>Pueraria thunbergiana</i> ).	36.0140	1.3133	0.6026	0.5502
6. Cow-dung ...	9.8000	5.2419	0.6107	0.5409
7. Oil-cake ...	35.4500	0.5242	0.5452	0.4940

*(b) Alkaline soil*

Mean temperature during exposure—32°

Date of starting the experiment 2—2—52.

TABLE 4

*Nitrate nitrogen*

Material used	Nitrogen content of the material added	Weight of the material added to 500 gms soil	Nitrate nitrogen in the leachings	Gain or loss of nitrogen (nitrate)
	%	gms.	m. gms.	m. gms.
1. Control soil ...	0.0334	...	12.3	...
2. Lignite ...	0.5600	4.2180	5.2	- 7.1
3. Wheat straw ...	1.0410	2.2690	9.0	- 3.3
4. Clover ...	1.7200	1.3733	10.6	- 1.7
5. Koodju ( <i>Puer- aria thunber- giana</i> ).	1.8000	1.3133	11.8	- 0.5
6. Cow-dung ...	0.4500	5.2419	12.6	+ 0.3
7. Oil cake ...	4.5000	0.5242	14.7	+ 2.4

TABLE 5

*Total nitrogen*

Material used	Nitrogen content of the material added.	Weight of the material added to 500 gms. soil.	Total nitrogen before exposure.	Total nitrogen after exposure.
	%	gms.	%	%
1. Control soil ...	0.0334	...	0.0334	0.0301
2. Lignite ...	0.5600	4.2180	0.0376	0.0346
3. Wheat straw ...	1.0401	2.6690	0.0376	0.0370
4. Clover ...	1.7200	1.3733	0.0376	0.0380
5. Koodju ( <i>Puer- aria thunbergiana</i> ).	1.8000	1.3133	0.0376	0.0379
6. Cow-dung ...	0.4500	5.2419	0.0376	0.0396
7. Oil cake ...	4.5000	0.5242	0.0376	0.0390

TABLE 6

*Total Carbon*

Material used	Carbon content of the material.	Weight of the material added to 500 gms. soil.	Total carbon before exposure.	Total carbon after exposure.
	%	gms.	%	%
1. Control soil ...	0.1143	...	0.1143	0.1103
2. Lignite ...	60.0001	4.2180	0.6205	0.5704
3. Wheat straw ...	40.0000	2.2690	0.2958	0.2074
4. Clover ...	38.0198	1.3733	0.2188	0.1492
5. Koodju ( <i>Puer- aria thunbergiana</i> ).	36.0140	1.3133	0.2089	0.1468
6. Cow-dung ...	9.8000	5.2419	0.2170	0.1370
7. Oil cake ...	35.4500	0.5242	0.1515	0.0905

TABLE 7

*Normal soil*

Material used	Carbon before exposure.	Nitrogen before exposure	Carbon/ nitrogen ratio.	Carbon after exposure.	Nitrogen after exposure.	Efficiency (nitrogen fixed in mgm per gram. of carbon oxidized). m. gms.
	%	%		%	%	
1. Control soil	0.5080	0.0628	8.09	0.5040	0.0628	...
2. Lignite ...	1.0142	0.0670	14.25	0.9742	0.0673	7.5
3. Wheat straw	0.6895	0.0670	10.69	0.6101	0.0680	12.6
4. Clover ...	0.6125	0.0670	9.00	0.5527	0.0682	20.1
5. Koodju ( <i>Pueraria thunbergiana</i> )	0.6026	0.0670	8.86	0.5502	0.0679	17.2
6. Cow-dung...	0.6107	0.0670	14.54	0.5409	0.0732	88.8
7. Oil cake ...	0.5452	0.0670	8.03	0.4940	0.0692	42.9

TABLE 8

*Alkaline soil*

1. Control soil	0.1143	0.0334	3.42	0.1103	0.0301	...
2. Lignite ...	0.6205	0.0376	12.80	0.5704	0.0346	...
3. Wheat straw	0.2958	0.0376	6.09	0.2074	0.0370	...
4. Clover ...	0.2188	0.0376	5.57	0.1492	0.0380	5.7
5. Koodju ( <i>Pueraria thunbergiana</i> )	9.2089	0.0376	5.32	0.1468	0.0379	4.8
6. Cow-dung ...	0.2170	0.0376	15.43	0.1370	0.0396	25.0
7. Oil cake ...	0.1515	0.0376	3.85	0.0905	0.0390	22.9

The foregoing results show that with normal soil there has been an appreciable increase in total nitrogen with all the organic substances irrespective of their carbon/nitrogen ratio. Moreover in all these cases the nitrate-nitrogen has also appreciably increased after six months exposure to light. In these experiments which lasted for six months the organic matter has undergone oxidation more in the alkali soil than in the normal soil. These results clearly show that there is fixation of atmospheric nitrogen when organic matter with carbon/nitrogen ratio greater than 10 is allowed to undergo slow oxidation in air in contact with soil. These results are in agreement with those obtained by Dhar<sup>4</sup> and co-workers. With

alkali soils there has been slight decrease in nitrate-nitrogen in all cases except cow-dung and oil-cake where increase in nitrate nitrogen has been observed. The total nitrogen has increased with clover, Koodju (*Pueraria thunbergiana*), cow-dung and oil-cake though the total nitrogen have appreciably decreased with straw and lignite and in the original alkali soil. It is well known that the proteins present in the organic matters added to soil and those produced by fixation of atmospheric nitrogen undergo more marked decomposition and oxidation in alkali soils with high pH values than in normal soils. Hence there are greater amounts of total nitrogen and nitrate in the normal soil than alkali soil.

Lignite with a carbon/nitrogen ratio 107 is not as suitable for fixing atmospheric nitrogen as straw, clover, Koodju, cow-dung and oil-cake even in normal soils, although the carbon/nitrogen ratio of those materials are smaller than that of lignite. It seems that the carbonaceous materials present in lignite are more inert and difficultly oxidisable than these present in the plant residues. It seems, therefore, that difficultly oxidisable carbonaceous materials are not very suitable in inducing fixation of atmospheric nitrogen and retarding loss of nitrogen from nitrogenous compounds.

Dhar, Ghildyal, Agrawal and Francis<sup>5</sup> have shown that on adding 5.769 gms. of wheat straw to 500 grams of ordinary soil the total, nitrogen content of the system increases from 0.064% to 0.076% in 180 days exposure to sunlight, whilst on adding the same amount of lignite to 500 grams of the same soil, the total nitrogen drops from 0.0166% to 0.0119%. It appears, therefore, that straw is more suitable for nitrogen fixation than lignite in which loss of nitrogen is observed more readily than in straw.

It is clear, therefore, that the experiments performed by S. A. Waksman and F. G. Tenney, and their results do not represent a complete picture of the nitrogen transformation in the soil on the addition of organic matter of different carbon/nitrogen ratios. In order to obtain a true picture of the nitrogen transformations taking place in soils by incorporating organic matter it is necessary to determine the total nitrogen, nitrate nitrogen and total carbon of the system. Dhar and coworkers have emphasised that if adequate time interval is given between the addition of organic matter and sowing of a crop all organic substances with C/N ratio greater than 10, can increase land fertility by fixation of atmospheric nitrogen and this effect is intensified by light absorption and in calcium phosphate rich soils or to which calcium phosphate has been added. It has been frequently observed in this laboratory that oil-cake when mixed with alkali soils can reclaim such soils and there is an appreciable fixation of atmospheric nitrogen although the carbon/nitrogen ratio of oil cakes is less than 10. This is certainly due to the formation of the oleate, palmitate and stearate of sodium formed by the action of alkali present in the alkali soils on the oil contents of the oil cakes. Moreover it has also been observed that these salts of organic acids undergo very slow oxidation and fix atmospheric nitrogen slowly when mixed with soil. Some of the results obtained by Dhar<sup>6</sup> and coworkers are given below—

#### NITROGEN FIXATION IN THE OXIDATION OF SODIUM SALTS OF ORGANIC ACIDS

*Analysed on 14-3-36.*

Materials added to 200 grams of soil.	Ammonical nitrogen. %	Nitric nitrogen. %	Total nitrogen. %	Total carbon. %
1. Sodium stearate 10.8 gms	0.00186	0.00164	0.0458	4.384
2. Sodium palmitate 10.7 gms	0.00186	0.00164	0.0458	3.887
3. Sodium oleate 10.86 gms	0.00186	0.00164	0.0458	4.02

*Analysed on 16-7-36*

1. Sodium stearate 10.8 gms	0.0012	0.00194	0.0583	2.323
2. Sodium palmitate 10.7 gms	0.0019	0.00268	0.0540	2.212
3. Sodium oleate 10.86 gms	0.0014	0.00250	0.0534	2.452

In our experiments recorded in tables 1 to 8 we have also obtained similar results with oil cakes showing marked fixation of atmospheric nitrogen when mixed with both alkali and normal soil. Similarly with cow-dung also we have obtained a marked fixation of atmospheric nitrogen both in normal and alkali soils just as obtained by Dhar<sup>4</sup> and coworkers.

Therefore from our experiments it can be concluded that the value of cow-dung and oil cakes when added to soil depends not only on their contents of nitrogen, potassium, phosphates and other plant food materials but also to their ability in fixing atmospheric nitrogen and increase in soil fertility.

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# ROLE OF PHOSPHATE IN PLANTS

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In the present piece of investigation an attempt has been made to study the role of phosphate in the plants. The problem has been approached from the point of view of a Plant Physiologist. Here only the amount of phosphorus that has been actually taken up by the plants has been taken into account, because it is ultimately the amount of phosphorus present in the different organs of the plant and especially the leaves that will influence the metabolism of the plant which will in turn effect the growth and yield of the crop. We are, however, not directly concerned with the amount of total and available phosphorus present in the soil and the way it is made available to the plant. Thus, for the present, it is only the amount of phosphorus taken up by the plant which is of importance and need be considered.

Recent researches have established beyond doubt the importance of the role of phosphate in the plant kingdom and it has come to be realised that it plays a major role in all metabolic processes. In the present work a study of the effect of three major nutrients i.e., nitrogen, phosphorus and potassium applied to the soil, singly and in combination, on the amount of phosphate taken up by the barley plant (var. C. 251) as revealed by leaf analysis at different period of its life cycle and the relationship of leaf  $P_2O_5$  to the growth, yield and the uptake of nitrogen and potassium has been undertaken.

When varying doses of nitrogen fertilizer was applied and its effect on  $P_2O_5$  uptake was followed, it was observed that in the lower doses of nitrogen treatments there was an increase in  $P_2O_5$  uptake, but higher doses of nitrogen did not show corresponding increase on unit weight basis, due to increased vegetative growth as seen from growth record (Fig. 1 and 2). For phosphate accumulation in the leaves lower N doses proved more efficacious. This indicated that the application of nitrogen was helpful in phosphate uptake especially in the lower dosage series at earlier stages. Under the phosphorus treatment series the uptake of nitrogen also revealed favourable effect of phosphates on the nitrogen uptake. Gibes, Childers and Loustalot (1947) had also reported that P was required for the normal absorption and possibly the utilization of nitrogen by the plants. The increase in uptake of nitrogen in medium doses as compared to control at the heading stage (Fig. 1), further supported the view that  $P_2O_5$  favoured nitrogen uptake. Under combination treatments also it was seen that the NK treatment recorded higher  $P_2O_5$  values in the leaves than control which indicated that there was probably some beneficial effect of nitrogen application on phosphorus uptake (Fig. 3).

It was also seen that leaf  $P_2O_5$  behaved in more or less similar way as nitrogen did because there was a similarity between symptoms of phosphorus and nitrogen deficiency in respect to low meristematic activity as indicated by reduction in tillering, leaf production rate and leaf area of barley plant. According to Mac Gillvary (1927) high percentage of phosphorus is associated with regions of active growth and thus a lack of sufficient phosphorus leads to poor growth. Similar effect was also noticed in potassium treated plants where  $P_2O_5$  uptake was very low and there was consequently very poor growth.

## CORRELATIONS AT THE HEADING STAGE

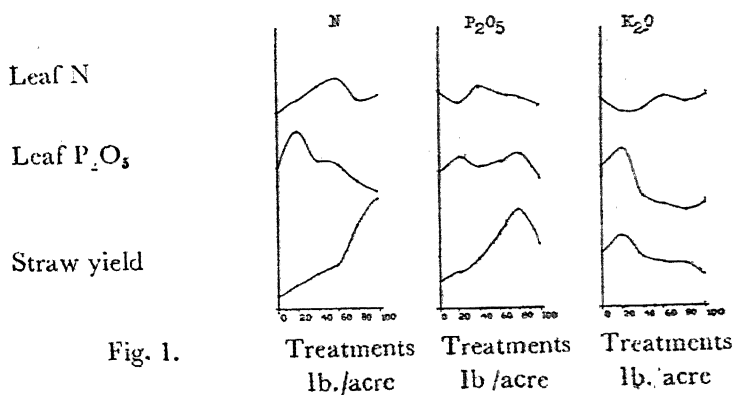


Fig. 1.

### CORRELATIONS AT THE MILKY GRAIN STAGE

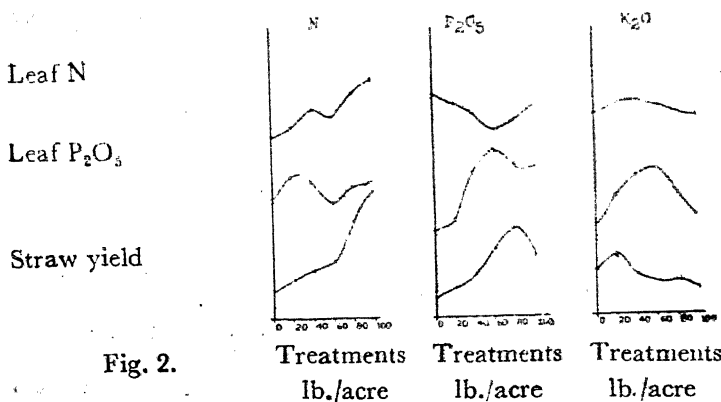


Fig. 2.

### CORRELATIONS UNDER N-P-K COMBINATIONS

(Singly and in combination at 40 lb. level)

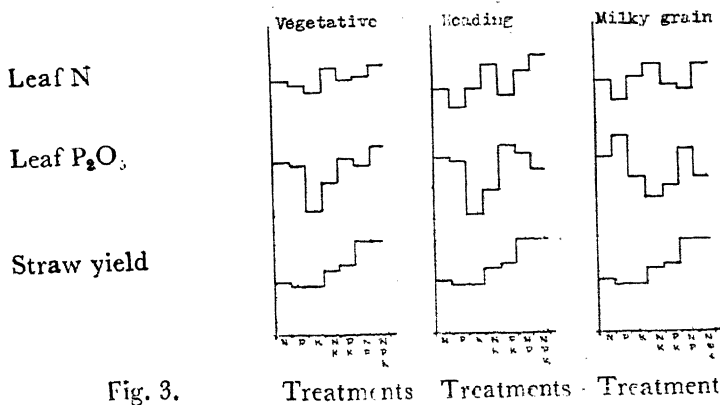


Fig. 3.

With increase in age the uptake of phosphorus showed a rise in all the treatments upto 70 days after which there was a decline except P and K which showed a rise. The rise in P treated plants after this stage seems to be in the region of luxury consumption because these treatments were in no way superior to the N treatments in which there was no more increase in  $P_2O_5$  uptake after this stage. Chapman (1935) also reported that oat plants absorb most of the potassium elements at the vegetative stage. It has also been reported by Gericke (1925) and Brenchley (1929) that wheat and barley take up much of their phosphate in early stages of growth and that starvation in early stages cannot be rectified by supply at a later stage.

Another interesting point which emerged out of the present investigation was that the leaf P at the heading stage showed a correlation with the straw yield in both the phosphorus and potassium series and also in the combination treatments. With increase in leaf P a corresponding increase in straw yield was recorded. This relationship was very well borne out with leaf P at the milky grain stage and straw yield. Contrary to the popular belief that it is the leaf N that controls the straw yield under the present investigations it is amply borne out that leaf P has a deciding influence upon straw yield; greater leaf P leading to greater straw production and *vice versa*. As phosphorus plays a positive role in metabolic processes, therefore a reduction in phosphorus leads to many of the physiological processes being retarded and consequently a fall in straw yield. When phosphorus is lacking no clear division takes place and meristematic activity is diminished.

Thus it is quite clear that from the point of view of a plant Physiologist the amount of phosphate taken up by the plant is of great importance in studying the role of phosphate in plants because it influences the uptake of other nutrients, plant growth, yield and also many of the physiological processes as indicated above.

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# RETARDING EFFECT OF LIGNITE AND DIFFERENT PHOSPHATES ON THE NITROGEN LOSS IN SOILS,

By

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The problem of nitrogen loss being intimately connected with that of nitrogen fixation is of fundamental importance to soil fertility. It is generally known that when artificial nitrogenous fertilizers like urea, ammonium sulphate, sodium nitrate etc. are added to the soil, whole of their nitrogen content is not utilized by the plants but a good deal of it is lost as nitrogen gas.

A large amount of research work has been carried out in this Institute on the problem of nitrogen loss on the addition of nitrogenous manures and fertilizers and the retardation of this loss by adding carbonaceous substances.

In this paper we have studied the retarding effect of adding lignite on the loss of nitrogen when different amounts of ammonium sulphate and sodium nitrate are added to the soil. The influence of eight different phosphates (mono, di, tri calcium phosphates, Iron, aluminium, magnesium, rock phosphate and basic slag from the Tatas) alone and with lignite has also been studied.

## Experimental procedure :

100 gms. of powdered soil after being passed through a sieve of 50 mesh, was taken in white enamelled dishes. Ammonium sulphate in two different doses (0.03% nitrogen and 0.1% nitrogen) and 0.1% nitrogen as sodium nitrate were added. 0.25%  $P_2O_5$  in the form of mono, di, tri calcium phosphate, iron, aluminium, magnesium phosphate, rock phosphate and basic slag was also added and the contents of the dishes were thoroughly mixed. Another set was kept with the addition of 0.5% carbon in the form of lignite in each dish containing 0.1% nitrogen as ammonium sulphate and sodium nitrate, alone and with different phosphates. Two such sets were taken—one to be exposed under an electric bulb of 100 watts at an approximate distance of  $2\frac{1}{2}$  feet, and the other to be covered with a thick black cloth to cut off light completely. The contents of the dishes were stirred well with a glass rod to facilitate aeration and about 20% of distilled water was added, daily to the exposed sets and every third day to the covered sets. Composite samples were taken at the time of analysis after completely powdering and drying. Total nitrogen was estimated by the Kjeldahl Salicylic acid reduction<sup>1</sup> method. In case of ammonium sulphate, carbon was estimated by the Robinson and McLean<sup>2</sup> method.

**Observations :—**

TABLE NO. 1

0.03% nitrogen as ammonium sulphate + 0.25 %  $P_2O_5$

Phosphate added		Nitrogen loss percentage.			
		60 days		180 days	
		Light	Covered	Light	Covered
No phosphate	...	54.2	46.7	70.2	60.6
Rock phosphate	...	41.9	34.1	54.5	46.4
Basic Slag	...	40.8	32.8	52.1	44.6
Mono Calcium phosphate	...	47.7	40.2	60.1	53.4
Di Calcium phosphate	...	43.9	36.2	53.8	48.7
Tri Calcium phosphate	...	41.6	33.8	52.9	45.7
Iron phosphate	...	49.4	41.8	62.7	55.6
Aluminium phosphate	...	50.1	42.5	63.5	56.1
Magnesium phosphate	...	46.4	38.6	58.7	52.1

TABLE NO. 2

0.1 % N as Ammonium Sulphate + 0.25 %  $P_2O_5$

Phosphate added		Nitrogen loss percentage			
		60 Days		180 Days	
		Light	Covered	Light	Covered
No phosphate	...	48.8	40.4	59.7	49.7
Rock phosphate	...	35.3	27.4	43.8	34.1
Basic slag	...	34.1	26.3	41.1	32.0
Mono Calcium phosphate	...	42.1	34.1	52.7	43.1
Di Calcium phosphate	...	38.2	29.5	48.6	37.9
Tri Calcium phosphate	...	35.1	27.2	42.9	34.8
Iron phosphate	...	43.9	36.4	54.8	45.6
Aluminium phosphate	...	44.6	37.3	56.2	47.1
Magnesium phosphate	...	40.9	32.3	50.3	40.5

TABLE NO. 3

0.1% N as Ammonium Sulphate + 0.5 % C as lignite + 0.25 %  $P_2 O_5$ 

Phosphate added		Nitrogen loss percentage			
		60 Days		180 Days	
		Light	Covered	Light	Covered
No phosphate	...	38.6	29.9	47.5	36.5
Rock phosphate	...	27.8	20.1	34.5	25.2
Basic slag	...	26.8	19.1	32.3	23.6
Mono Calcium phosphate	...	32.1	24.4	39.3	31.2
Di Calcium phosphate	...	29.9	22.3	35.8	27.6
Tri Calcium phosphate	...	27.7	19.9	34.8	24.5
Iron phosphate	...	33.5	25.9	43.2	32.9
Aluminium phosphate	...	34.3	26.4	44.5	33.8
Magnesium phosphate	...	30.6	23.6	38.1	29.3

TABLE NO. 4

0.1 % N as Sodium Nitrate + 0.25 %  $P_2 O_5$ 

Phosphate added		Nitrogen loss percentage			
		60 Days		180 Days	
		Light	Covered	Light	Covered
No phosphate	...	27.7	19.8	36.3	26.9
Rock phosphate	...	18.4	10.7	24.4	14.4
Basic slag	...	16.9	9.3	22.1	12.3
Mono Calcium phosphate	...	23.0	15.1	30.3	20.6
Di Calcium phosphate	...	19.8	12.1	26.3	16.0
Tri Calcium phosphate	...	18.1	10.3	23.7	11.5
Iron phosphate	...	25.1	17.0	32.7	22.4
Aluminium phosphate	...	25.6	17.4	33.8	23.0
Magnesium phosphate	...	21.3	13.3	28.5	19.1

TABLE NO. 5

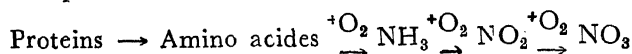
0.1 % N as Sodium Nitrate + 0.5 % C as lignite + 0.25 %  $P_2O_5$ 

Phosphate added		Nitrogen loss percentage			
		60 Days		180 Days	
		Light	Covered	Light	Covered
No phosphate	...	22.3	14.4	30.6	20.7
Rock phosphate	...	15.0	8.8	20.1	11.6
Basic slag	...	13.7	7.2	17.1	9.6
Mono Calcium phosphate	...	18.8	11.8	23.9	15.9
Di Calcium phosphate	...	16.2	9.4	21.0	13.1
Tri Calcium phosphate	...	14.8	8.1	19.2	10.5
Iron phosphate	...	20.1	12.8	26.6	17.8
Aluminium phosphate	...	20.9	13.1	27.7	18.5
Magnesium phosphate	...	17.3	10.6	23.1	14.6

## DISCUSSION

From a close study of the above results it is clear that both ammonium sulphate and sodium nitrate suffer losses when added to the soil. The loss is very quick in the beginning, but the rate slows down with time. Thus from table No. 1, we see that the loss in 60 days in case of 0.03 % nitrogen as ammonium sulphate is 54.2 % in light and 46.7 % in dark, while in 180 days it has increased only to 70.2 % in light and 60.6 % in dark. It is also clear that the loss is greater in light than in dark in all the cases as it evident from the above five tables. This clearly shows that it is not only microbiological, but also a photochemical reaction.

From tables 1 and 2, we see that the loss is greater in case of 0.03 % nitrogen than in case of 0.1 % nitrogen. This is due to the fact that in the former case there is greater amount of surface per unit weight of ammonium salt. In the latter case, the concentration of ammonium sulphate per unit area is greater resulting in smaller loss. Table 2 and 4 show that the loss is greater in case of ammonium sulphate while much smaller in case of sodium nitrate. According to Dhar<sup>4</sup>, the loss is due to the formation of ammonium nitrate as intermediate compound. The oxidation takes place as:—



Due to nitrification, the loss is greater in case of ammonium sulphate. In case of sodium nitrate, which is already in nitrate condition, there is no nitrification, but some reaction with soil humus takes place, thus reducing it to nitrite and ammonia, forming some ammonium nitrite which leads to the loss of nitrogen.

Addition of lignite appreciably checks the loss. The retarding effect can be explained on the basis that lignite acts as negative catalyst. It is well known that carbohydrates preserve body proteins from undergoing oxidation and it is just likely that carbonaceous matter present in the soil may act in such a way as to pro-

tect the soil protein and the nitrogenous material from oxidation. It is probable that lignite may adsorb some ammonia and thus retard its loss, as coals and lignites possess great adsorbing capacity for gases.

The retarding influence of phosphates is also very appreciable. Basic slag, rock phosphate, dicalcium phosphate, tricalcium phosphate and magnesium phosphate check the loss of nitrogen from the system appreciably. Monocalcium phosphate also checks the loss but, only to a smaller degree in comparison with other phosphates mentioned above. Iron and aluminium phosphates have very little retarding effect.

The effect of phosphates may be explained from the view point that calcium phosphates, rock phosphate, basic slag and magnesium phosphate furnish soluble Ca and Mg ions in the system to form nitrites which are more stable than ammonium nitrite, with the consequence that there is decrease in the loss of nitrogen. Ghosh<sup>3</sup> showed that addition of potassium chloride checks the loss of nitrogen due to the formation of more stable  $\text{KNO}_2$  than  $\text{NH}_4\text{NO}_2$  which is very unstable and breaks to liberate nitrogen gas resulting in great loss. Moreover it is probable that phosphates may form some stabler kind of phosphoproteins etc. which are more resistant to oxidation.

The fixation of nitrogen and nitrogen loss go side by side, and the loss is prominent when it exceeds the fixation. It has been shown clearly by Dhar and coworkers that phosphates markedly enhance the efficiency of nitrogen fixation i. e. the nitrogen fixed in mgms per gram of carbon oxidized, which goes a long way in neutralizing the loss. Hence the loss of nitrogen is lesser as observed.

It may therefore be concluded that the incorporation of phosphates and organic matter with nitrogenous fertilizers is a greatly beneficial process for the improvement of the nitrogen of the soil.

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# INFLUENCE OF NITRIFICATION ON THE AVAILABILITY OF PHOSPHATE

By

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The fertility of soil depends not only on the total amount of the various nutrients present, but also on the ease with which they are made available in an assimilable form. The availability of the different nutrients present in soil is governed by a large number of factors and an interaction between them exerts a most remarkable influence on the availability.

Phosphate is one of the most important nutrients. Van Hise<sup>1</sup> has stated "The problem of the conservation of our phosphates is the most crucial, the most important, the most far reaching with reference to the future of this nation of any of the problems of conservation." It has been reported<sup>2</sup> that phosphate deficiency is very wide spread in the world and many countries viz. South Africa, Australia, New Zealand crop production is limited over enormous areas by phosphate supply. The phosphate problem of primary agricultural importance concerns the availability of this very important plant nutrient to the plant root and its fixation when water soluble phosphates are added to the soil. The recovery of  $P_2O_5$  added in fertilizers rarely exceeds 20%. The nitrogenous and phosphatic fertilizers are often applied to the soil together, with a view to rectify the deficiency of both the elements. Thus an interaction between these two elements deserves a careful consideration in order to determine their ultimate benefit to the plant.

In view of the above fact, we have, in this paper, studied the effect of nitrogen loss, when ammonium sulphate is added to the soil, on the availability of  $P_2O_5$  of eight different phosphates including rock phosphate from Trichnopoly and basic slag from the Tatas.

*Experimental procedure*:—100 gms of well dried and powdered garden soil (sieved through a 50 mesh sieve) was taken in shallow enamel dishes. Nitrogen was added in two different doses of 0.03 % and 0.1 % in the form of ammonium sulphate. Eight different phosphates viz; mono, di and tri calcium phosphates, iron, aluminium, magnesium and rock phosphates and basic slag were added to give 0.25 %  $P_2O_5$ . The contents of the dishes were mixed thoroughly to make them completely homogeneous. The dishes were exposed to the light of an electric bulb of 100 watts, hung at an approximate distance of  $2\frac{1}{2}$  feet. The soil mixture was stirred every alternate day to facilitate the oxidation and about 20 % of distilled water was added. At the time of analysis, samples were taken after thoroughly mixing and completely drying the contents. Available phosphate was estimated by Dyer's method using 2 % citric acid solution.

TABLE No 1

0.03 % N as ammonium sulphate + 0.25 %  $P_2O_5$ 

Phosphate added				Available phosphate percentage		
				0 days	60 days	180 days
No phosphate	...	...	...	0.0311	0.0326	0.0348
Rock phosphate (Tata)	...	...	...	0.0365	0.0566	0.0825
Basic slag	...	...	...	0.1686	0.1997	0.2051
Mono Calcium phosphate	...	...	...	0.2211	0.1892	0.1833
Di Calcium phosphate	...	...	...	0.1846	0.1860	0.1909
Tri Calcium phosphate	...	...	...	0.1386	0.1582	0.1801
Iron phosphate	...	...	...	0.1683	0.1674	0.1683
Aluminium phosphate	...	...	...	0.1761	0.1746	0.1721
Magnesium phosphate	...	...	...	0.2036	0.2063	0.2111

TABLE No. 2

0.0 % N as ammonium sulphate + 0.25 %  $P_2O_5$ 

Phosphate added				Available $P_2O_5$ percentage		
				0 days	60 days	180 days
No phosphate	...	...	...	0.0311	0.0346	0.0368
Rock phosphate (Tata)	...	...	...	0.0365	0.0586	0.0879
Basic slag	...	...	...	0.1680	0.2022	0.2162
Mono Calcium phosphate	...	...	...	0.2211	0.1860	0.1808
Di Calcium phosphate	...	...	...	0.1846	0.1876	0.1929
Tri Calcium phosphate	...	...	...	0.1378	0.1616	0.1824
Iron phosphate	...	...	...	0.1676	0.1666	0.1652
Aluminium phosphate	...	...	...	0.1761	0.1729	0.1715
Magnesium phosphate	...	...	...	0.2036	0.2078	0.2129

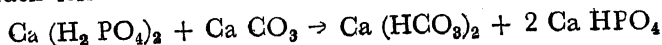
*Discussion.*—The above table shows that there is a definite increase in the availability of phosphate with lapse of time, when ammonium sulphate is added to the soil. This indicates that the presence of nitrogen is conducive to phosphate availability. This may be due to the fact that  $HNO_2$  and  $HNO_3$  produced during the process of nitrification of ammonium sulphate exert a solvent action upon the phosphorous compounds, thereby augmenting its availability to a considerable extent. Kelley<sup>3</sup>, Shrikhande<sup>4</sup> and Yadav have also arrived at similar conclusions.

On a close perusal of the above results we observe that there is more increase of availability in the case when 0.1 % N as ammonium sulphate is added than in case of 0.03 % nitrogen, though percentage loss of nitrogen is more in the latter case. This can be easily explained as the amount of acid produced is greater in the former case.

The most appreciable increases in phosphorus availability are in cases of tricalcium phosphate, rock phosphate and basic slag. This is certainly due to the conversion of the tricalcium phosphate present in rock phosphate and basic slag to more available dicalcium phosphate and small amounts of monocalcium phosphate. The nitrous and nitric acids formed in the conversion of ammonium in the process of nitrification reacts with the sparingly soluble tricalcium phosphate and monocalcium phosphate leads to the formation of more soluble dicalcium phosphate. It is interesting to note that the increase in availability in case of dicalcium phosphate is much less pronounced. This is due to the fact that the conversion of dicalcium phosphate to the monocalcium state in the presence of acids is much more difficult than the conversion of tricalcium phosphate to dicalcium phosphate. In case of rock phosphate, the initial availability is very low i.e. about 2 % but it increases very much i.e. upto about 20 %.

The availability of phosphate does not increase at all when iron and aluminium phosphates are added, but it has decreased a little. This may be due to the fact that there is little effect of acids on the availability of these two phosphates. Fujiwara<sup>5</sup> has explained the decrease of availability in case of iron and aluminium phosphates due to dehydration and ageing.

In case of monocalcium phosphate, the available phosphate which is high in the beginning decreases in course of time. This is due to the fact that monocalcium phosphate reacts with calcium carbonate present in the soil to produce dicalcium phosphate, which is much less soluble.



Hence we are of the opinion that basic slag, which is not being used in India, at present can go a long way in increasing the available phosphate status of our soils, thus saving the superphosphate, in view of the shortage of sulphur. Moreover, the  $\text{P}_2\text{O}_5$  in super phosphate is in the form of monocalcium phosphate, which, as we have seen, reverts in course of time to less soluble phosphates.

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# EFFECT OF MINERAL PHOSPHATES ON NITROGEN FIXATION EFFECTED BY THE OXIDATION OF LUCERNE PLANT

By

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The present study deals with the effects of fine mineral phosphates on the photo-chemical nitrogen fixation, carbon oxidation and Azotobacter population of a soil.

## EXPERIMENTAL

200 gms of the soil were taken in white enamelled dishes of seven inches diameter. 0.5% carbon was introduced in the form of dry, powdered lucerne plant. The various phosphates corresponding to their 0.1%  $P_2O_5$  content were also added. Moisture was maintained at 20% throughout. Two exactly similar sets were prepared, one was exposed to the artificial light from a 500 watt electric bulb and the other set was covered with a thick black cloth and placed beside the exposed set. Total carbon was estimated by Robinson, McLeans and Williams' method, total nitrogen by the kjeldahl salicylic acid reduction method while Azotobacter counts were made with Beijerinck's medium. Chemical analysis of lucerne plant and the soil used in these experiments are as follows:—

	Lucerne	Soil
Moisture =	10.3%	2.6%
Ash =	10.45%	—
Sesquioxides =	0.3%	11.2%
CaO =	1.68%	0.9834%
K <sub>2</sub> O =	3.42%	0.7496%
P <sub>2</sub> O <sub>5</sub> =	0.721%	0.0745%
Total Carbon =	42.06%	0.4022%
Total Nitrogen =	2.09%	0.0398%
Azotobacter in		
millions per gm. of soil=	—	2.0

Average Temp. = 26°C

TABLE No. 1

200 gms. of soil + 0.5% Carbon as lucerne.

Period of exposure in days.	Total carbon%	Total nitrogen%	Carbon oxidised%	Increase in nitrogen%	Efficiency (amount of nitrogen fixed in mgm. per gram of carbon oxidized)	Azotobacter millions per gm.
<i>Exposed</i>						
0	0.9011	0.0643	—	—	—	2.0
180	0.6584	0.0743	0.2427	0.0100	41.2	4.5
<i>Covered</i>						
0	0.9015	0.0644	—	—	—	2.0
180	0.7125	0.0682	0.1890	0.0038	20.1	7.6

TABLE No. 2

200 gms. of soil + 0.5% carbon as lucerne + 0.1%  $P_2O_5$  as monocalcium phosphate.

<i>Exposed</i>						
0	0.9003	0.0638	—	—	—	2.2
180	0.6508	0.0763	0.2493	0.0125	50.1	4.4
<i>Covered</i>						
0	0.9010	0.0640	—	—	—	2.0
180	0.6996	0.0691	0.2014	0.0051	25.3	6.9

TABLE No. 3

200 gms. of soil + 0.5% carbon as lucerne + 0.1%  $P_2O_5$  as dicalcium phosphate.

<i>Exposed</i>						
0	0.9020	0.0644	—	—	—	2.0
180	0.6466	0.0800	0.2554	0.0156	61.0	7.9
<i>Covered</i>						
0	0.9011	0.0644	—	—	—	2.0
180	0.6947	0.0707	0.2071	0.0063	30.4	11.0

TABLE No. 4

200 gms. of soil + 0.5% carbon as lucerne + 0.1%  $P_2O_5$  as tricalcium phosphate.

Period of exposure in days.	Total carbon%	Total nitrogen%	Carbon oxidised%	Increase in nitrogen%	Efficiency (amount of nitrogen fixed in mgm. per gram of carbon oxidized)	Azotobacter millions per gm.
<i>Exposed</i>						
0	0.9015	0.0642	—	—	—	2.0
180	0.6401	0.0789	0.2614	0.0147	56.2	7.4
<i>Covered</i>						
0	0.9003	0.0637	—	—	—	2.0
180	0.6882	0.0697	0.2121	0.0050	28.2	9.5

TABLE No. 5

200 gms. of soil + 0.5% carbon as lucerne + 0.1%  $P_2O_5$  as iron phosphate.

<i>Exposed</i>						
0	0.9028	0.0648	—	—	—	2.0
180	0.6582	0.0751	0.2446	0.0103	42.1	5.0
<i>Covered</i>						
0	0.9022	0.0643	—	—	—	2.0
180	0.7122	0.0684	0.1900	0.0041	21.5	8.0

TABLE No. 6

200 gms. of soil + 0.5% carbon as lucerne + 0.1%  $P_2O_5$  as Aluminium phosphate.

<i>Exposed</i>						
0	0.9008	0.0637	—	—	—	2.0
180	0.6591	0.0740	0.2407	0.0103	4.27	4.5
<i>Covered</i>						
0	0.9031	0.0649	—	—	—	2.0
180	0.7117	0.0692	0.1914	0.0043	22.4	7.4

## DISCUSSION

A careful examination of the above results show that when organic matter in the form of lucerne plant is mixed with soil and allowed to undergo slow oxidation in the air, nitrogen of the atmosphere is fixed. The fixation in light is always greater than that in dark. It is practically double in light.

The addition of phosphates increases the oxidation of carbonaceous matter. The highest oxidation is obtained with tricalcium phosphate and this is perhaps due to the alkaline nature of tricalcium phosphate. It is well known that alkali helps in the oxidation of carbonaceous matter. The order in which the above phosphates increase the oxidation is  $\text{Ca}_3(\text{PO}_4)_2 > \text{CaHPO}_4 > \text{Ca}(\text{H}_2\text{PO}_4)_2 > \text{FePO}_4 > \text{AlPO}_4$ . Furthermore, these phosphates markedly increase the nitrogen fixation. The order in which these phosphates enhance the efficiency of nitrogen fixation is slightly different from that of increase in oxidation. The order is  $\text{CaHPO}_4 > \text{Ca}_3(\text{PO}_4)_2 > \text{Ca}(\text{HPO}_4)_2 > \text{FePO}_4 > \text{AlPO}_4$ . Monocalcium phosphate which is distinctly acidic in reaction shows a lesser efficiency than di and tricalcium phosphates. Ferric and aluminium phosphates increase the efficiency of nitrogen fixation only to a slight extent.

These phosphates may form stabler phosphoproteins which resist nitrification. The incorporation of calcium phosphate introduces calcium ion into the system and this might be forming calcium nitrite by reacting with ammonium nitrite. This calcium nitrite is stabler than ammonium nitrite. Moreover, as the decomposition of ammonium nitrite is catalysed by acids, the buffering action of di and tri phosphates does not allow the increase in the hydrogen ion concentration in the system during the course of oxidation of organic compounds and so this results in the checking of loss or increase in efficiency.

The determination of the azotobacter numbers shows that dicalcium phosphate, tricalcium phosphate and ferric phosphate stimulate azotobacter growth. Monocalcium and aluminium phosphates, on the other hand suppress the growth of azotobacter. It is well known that aluminium can be poisonous to soil microflora. The suppressing effect of monocalcium phosphate is perhaps due to its acidity.

The number of azotobacter is always smaller in light than in dark. But the fixation of nitrogen is always greater in sets exposed to light than in sets covered with black cloth. This clearly brings out the fact that azotobacter have not much to do with the process of nitrogen fixation.

# EFFECTS OF DICALCIUM PHOSPHATE AND ORGANIC MATTER ON NITROGEN LOSS IN SOILS

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Nitrogen is being continuously lost from soils, under cultivation and from soils to which synthetic fertilizers or organic nitrogenous compounds are added and also from virgin soils which are only broken for cropping.

According to Dhar and coworkers, ammonia or ammonium salt when being nitrified is converted into nitrite at one stage and this along with the free ammonium ion present, forms ammonium nitrite which rapidly decomposes with loss of nitrogen on account of its instability. In this communication, a systematic study of the problem of this loss and its retardation by lucerne and dicalcium phosphate has been made.

## EXPERIMENTAL

200 grams of soil were taken in white enamelled dishes of seven inches diameter. 1·888 grams of powdered lucerne plant was added to introduce 0·5% carbon, 0·1%  $P_2O_5$  as dicalcium phosphate and 0·1 % nitrogen as urea, ammonium sulphate and sodium nitrate were also added. One such set was exposed to artificial light from 500 watt electric bulb and the other similar set was covered with a thick black cloth and placed beside the exposed set. Moisture was maintained throughout at 20%. Total nitrogen was estimated by salicylic acid reduction method and carbon by Robinson, McLeans and Williams method. Chemical analysis of the lucerne plant and the soil used in these experiments :—

	Soil	Lucerne
Silica =	80·2%	—
Moisture =	2·6%	10·3%
Sesquioxides =	11·2%	0·3%
CaO =	0·9834%	1·68%
K <sub>2</sub> O =	0·7496%	3·42%
P <sub>2</sub> O <sub>5</sub> =	0·0745%	0·721%
Total Carbon =	0·4022%	42·06%
Total nitrogen =	0·0398%	2·09%

Average Temp. 30°

TABLE No. 1

200 gms. of soil + 0.1% nitrogen as Urea.

Period of exposure in days.	Total carbon %	Total nitrogen %	Nitrogen Loss %
	<i>Exposed</i>		
0	0.4021	0.1398	—
60	0.3818	0.0816	58.2
120	0.3745	0.0751	64.7
	<i>Covered</i>		
0	0.4021	0.1398	—
60	0.3921	0.0927	47.1
120	0.3881	0.0874	52.4

TABLE No. 2

200 gms. of soil + 0.1% nitrogen as Urea + 0.5%  
carbon as lucerne.

	<i>Exposed</i>		
0	0.9022	0.1646	—
60	0.7449	0.1174	47.2
120	0.6817	0.1125	52.1
	<i>Covered</i>		
0	0.9025	0.1647	—
60	0.7889	0.1253	39.4
120	0.7478	0.1212	43.5

TABLE No. 3

200 gms. of soil + 0.1% nitrogen as Urea + 0.5% carbon as lucerne + 0.1%  $P_2O_5$   
as dicalcium phosphate.

	<i>Exposed</i>		
0	0.9018	0.1645	—
60	0.7372	0.1229	41.6
120	0.6724	0.1203	44.2
	<i>Covered</i>		
0	0.9015	0.1643	—
60	0.7801	0.1352	29.1
120	0.7214	0.1313	33.0

TABLE No. 4

200 gms. of soil + 0.1% nitrogen as ammonium sulphate.

	<i>Exposed</i>		
0	0.4021	0.1398	—
60	0.3822	0.0856	54.2
120	0.3757	0.0780	61.8
	<i>Covered</i>		
0	0.4021	0.1398	—
60	0.3941	0.0976	42.2
120	0.3891	0.0924	47.4

TABLE No. 5

200 gms. of soil + 0.1% nitrogen as ammonium sulphate + 0.5%  
carbon as lucerne

<i>Exposed</i>			
0	0.9028	0.1648	—
60	0.7472	0.1205	44.3
120	0.6836	0.1162	48.6
<i>Covered</i>			
0	0.9021	0.1646	—
60	0.7900	0.1288	35.8
120	0.7489	0.1254	39.2

TABLE No. 6

200 gms. of soil + 0.1% nitrogen as ammonium sulphate + 0.5%  
carbon as lucerne + 0.1%  $P_2O_5$  as dicalcium phosphate.

<i>Exposed</i>			
0	0.9020	0.1644	—
60	0.7378	0.1298	34.6
120	0.6738	0.1262	38.2
<i>Covered</i>			
0	0.9026	0.1646	—
60	0.7803	0.1395	25.1
120	0.7388	0.1358	28.8

TABLE No. 7

200 gms. of soil + 0.1% nitrogen as sodium nitrate.

<i>Exposed</i>			
0	0.4021	0.1398	—
60	0.3819	0.1081	31.7
120	0.3750	0.1006	39.2
<i>Covered</i>			
0	0.4021	0.1398	—
60	0.3837	0.1158	24.0
120	0.3759	0.1100	29.8

TABLE No. 8

200 gms. of soil + 0.1% nitrogen as sodium nitrate + 0.5% carbon as lucerne.

<i>Exposed</i>			
0	0.9021	0.1646	—
60	0.7445	0.1413	23.3
120	0.6801	0.1330	31.6
<i>Covered</i>			
0	0.9024	0.1646	—
60	0.7881	0.1482	16.4
120	0.7462	0.1424	22.2

TABLE No. 9

200 gms. of soil + 0.1% nitrogen as sodium nitrate + 0.5% carbon as  
lucerne + 0.1%  $P_2O_5$  as dicalcium phosphate.

<i>Exposed.</i>			
0	0.9019	0.1646	...
60	0.7344	0.1484	16.2
120	0.6720	0.1432	21.4
<i>Covered</i>			
0	0.9010	0.1644	...
60	0.7782	0.1523	12.1
120	0.7362	0.1496	14.8

## DISCUSSION

It is evident from the above results that the major portion of the nitrogen added to the soil in the form of urea is lost. This loss is rapid in the beginning but with lapse of time it slows down. In the case of sodium nitrate, the loss of nitrogen is less pronounced than with urea or ammonium sulphate.

Organic matter in the form of lucerne plant partially checks the loss in all the three soils. This can be explained from the view point of negative catalysis, as the retarding influence of the carbonaceous substances like cellulose, carbohydrates and fats added with organic manure upon the oxidation of proteins, amino acids and ammonium salts.

In every case there is greater loss in sets exposed to light than in covered sets. This shows that light plays an important part in denitrification. Had it been only bacterial denitrification, losses would have been greater in covered sets which invariably contain greater bacterial population.

Best results were obtained by the authors with the mixture of organic matter and dicalcium phosphate. Phosphates may retard the loss in three ways. Firstly they may form stabler phosphoproteins which undergo nitrification more slowly than proteins alone. Secondly, as phosphates markedly increase nitrogen fixation; and since observed loss is the balance of total nitrogen losses occurring and nitrogen fixation going on side by side, some loss in this case may be made good by this greater fixation and the net result appears to be a checking effect on the loss of nitrogen. Thirdly, the calcium ion introduced into the system by the addition of calcium diphosphate which is slightly soluble in water may react with ammonium nitrite to give calcium nitrite which is more stable than ammonium nitrite.

## SUMMARY

When urea, ammonium sulphate and sodium nitrate are added to the soil, a loss of nitrogen ensues. Urea suffers the maximum loss while sodium nitrate suffers the minimum. Addition of lucerne plant partially checks this loss but the best results are obtained with a mixture of organic matter and dicalcium phosphate. The loss is always more pronounced in light than in dark.



# ADSORPTION OF PHOSPHATE BY TITANIUM DIOXIDE AND ILMENITE

By

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The reactions of phosphates with colloids, precipitates, minerals and soils have been studied extensively during recent years. Voelcker<sup>1</sup> showed that a sample of clay soil containing only a small percentage of calcium carbonate was active in phosphate adsorption and concluded that this was partially due to formation of insoluble compounds with the hydrous iron and aluminium oxides present in the soil and also to the precipitation of calcium phosphate. Warington<sup>2</sup> observed the retention of phosphate from solutions by precipitated hydrous ferric and aluminium oxides and he stated that the reaction was chemical in nature and resulted in the formation of ferric and aluminium phosphates.

In the last thirty years a detailed study of the mechanism of phosphate fixation has been made. Most of the work has been directed to the elucidation of the part played by the oxides of iron and aluminium. It is now established that under the conditions that exist in soil, iron and aluminium hydroxides adsorb phosphate ions. In some cases the phosphate ions are considered to be attacking merely the surface of hydrated oxides of iron and aluminium and in other cases a definite compound is believed to be formed. Rathje<sup>3</sup> found that the maximum precipitation of phosphate by an excess iron was at pH 3.0 and with aluminium at pH 4.0.

The reactions of phosphate with the sesquioxides of iron and aluminium either in solution or chemical precipitation or by surface adsorption have been considered to be an important factor in the fixation of phosphate in soil. The work of Gaarder<sup>4</sup> indicates that the pH values of the soils play an important part in influencing the form in which the phosphate is fixed by the soil. Besides iron and aluminium, manganese and titanium may be active in the fixation of phosphate. Raychaudhuri and Mukerjee<sup>5</sup> have studied the rate of uptake of phosphate from a solution of  $\text{KH}_2\text{PO}_4$  by ilmenite containing 46.97%  $\text{TiO}_2$  and 47.19%  $\text{Fe}_2\text{O}_3$ .

The present investigation has been undertaken with a view to obtain information as to the fixation of phosphate by titanium dioxide and ilmenite (containing 59.5%  $\text{TiO}_2$  and 39.0%  $\text{Fe}_2\text{O}_3$ ) in alkaline and acidic media.

In the following discussion the terms adsorption, retention and fixation have been used synonymously and denote the removal of phosphate from the solution.

## EXPERIMENTAL

Phosphate adsorption studies have been carried on with A. R. quality of  $\text{TiO}_2$  and ilmenite, (a mineral containing 59.5% of  $\text{TiO}_2$  and 39.0% of  $\text{Fe}_2\text{O}_3$ ) which has been obtained from Travancore-Cochin (India). The  $\text{TiO}_2$  and ilmenite were passed through a 80 mesh sieve, after being powdered. The mineral ilmenite was first analysed for its constituents by the procedure described by Washington<sup>6</sup>.

The experiments were performed at  $30^\circ \pm 0.1^\circ\text{C}$  at 1.00, 0.50, 0.25, 0.20, 0.10, 0.04, 0.02 and 0.01 molar solutions of  $\text{K}_3\text{PO}_4$ ,  $\text{K}_2\text{HPO}_4$ ,  $\text{KH}_2\text{PO}_4$ ,  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{H}_3\text{PO}_4$ . 0.5 g. of air dried samples of  $\text{TiO}_2$  and ilmenite were taken

in several 150 ml. Jena glass bottles and 40 ml. of the phosphate solutions were added. The contents were shaken for one hour in a mechanical shaker and then allowed to stand for 24 hrs at  $30^{\circ} \pm 0.1^{\circ}\text{C}$ . After 24 hrs the solutions were filtered and in suitable aliquot portions the phosphate was estimated. The amount of titanium in the molar phosphoric acid as  $\text{TiO}_2$  dissolved in concentrated  $\text{H}_3\text{PO}_4$  solution was also estimated. The pH of the solutions used for adsorption as well as of the supernatant liquids after adsorption were also measured.

*Determination of phosphate:*—The phosphate was estimated volumetrically after precipitating it with ammonium molybdate by the procedure described by Vogel<sup>7</sup>.

*Determination of titanium:*—The titanium was estimated colorimetrically with a Klett—Summerson Photoelectric colorimeter using filter KS 42 and hydrogen peroxide as colorimetric reagent.

*pH measurement:*—pH measurements were made with Leeds Northrup's A-C operated pH meter using glass electrode and a saturated calomel electrode.

The results are recorded in the following tables:—

TABLE No. 1.

Adsorption of phosphate by  $\text{TiO}_2$  from  $\text{K}_3\text{PO}_4$  solution at pH 12.5 to 11.6

Original concentration of the solution (molar)	Equilibrium concentration (molar)	Amount of $\text{P}_2\text{O}_5$ adsorbed by 0.5 g. (in g.)
1.00	0.9820	0.0509
0.50	0.4921	0.0266
0.25	0.2454	0.0138
0.20	0.1957	0.0122
0.10	0.0976	0.0062
0.04	0.0390	0.0027
0.02	0.0194	0.0015
0.01	0.0096	0.0009

TABLE No. 2.

Adsorption of phosphate by ilmenite from  $\text{K}_3\text{PO}_4$  solution at pH 12.5 to 11.6

Original concentration of the solution (molar)	Equilibrium concentration (molar)	Amount of $\text{P}_2\text{O}_5$ adsorbed by 0.5 g. (in g.)
1.00	0.9775	0.0638
0.50	0.4813	0.0332
0.25	0.2431	0.0175
0.20	0.1948	0.0145
0.10	0.0975	0.0071
0.04	0.0389	0.0029
0.02	0.0194	0.0016
0.01	0.0096	0.0009

TABLE No. 3.

Adsorption of phosphate by  $\text{TiO}_2$  from  $\text{K}_2\text{HPO}_4$  solution at pH 8.88 to 8.10.

Original concentration of the solution (molar)	Equilibrium concentration (molar)	Amount of $\text{P}_2\text{O}_5$ adsorbed by 0.5 g. (in g.)
1.00	0.9748	0.0715
0.50	0.4849	0.0425
0.25	0.2420	0.0225
0.20	0.1934	0.0185
0.10	0.0955	0.0098
0.04	0.0386	0.0038
0.02	0.0192	0.0021
0.01	0.0096	0.0012

TABLE No. 4.

Adsorption of phosphate by ilmenite from  $\text{K}_2\text{HPO}_4$  solution at pH 8.88 to 8.10

Original concentration of the solution (molar)	Equilibrium concentration (molar)	Amount of $\text{P}_2\text{O}_5$ adsorbed by 0.5 g. (in g.)
1.00	0.9685	0.0890
0.50	0.4816	0.0520
0.25	0.2402	0.0276
0.20	0.1924	0.0215
0.10	0.0958	0.0118
0.04	0.0384	0.0045
0.02	0.0190	0.0027
0.01	0.0094	0.0015

TABLE No. 5.

Adsorption of phosphate by  $\text{TiO}_2$  from  $\text{KH}_2\text{PO}_4$  solution at pH 4.20 to 5.15

Original concentration of the solution (molar)	Equilibrium concentration (molar)	Amount of $\text{P}_2\text{O}_5$ adsorbed by 0.5 g. in g.
1.00	0.9818	0.0882
0.50	0.4717	0.0519
0.25	0.2403	0.0275
0.20	0.1917	0.0235
0.10	0.0948	0.0141
0.04	0.0380	0.0054
0.02	0.0189	0.0029
0.01	0.0094	0.0016

TABLE No. 6.

Adsorption of phosphate by ilmenite from  $\text{KH}_2\text{PO}_4$  solution at pH 4.20 to 5.15

Original concentration of the solution (molar)	Equilibrium concentration (molar)	Amount of $\text{P}_2\text{O}_5$ adsorbed by 0.5 g. in g.
1.00	0.9608	0.1115
0.50	0.4776	0.0636
0.25	0.2369	0.0371
0.20	0.1889	0.0315
0.10	0.0938	0.0174
0.04	0.0375	0.0069
0.02	0.0187	0.0037
0.01	0.0093	0.0020

TABLE No. 7.

Adsorption of phosphate by  $\text{TiO}_2$  from  $(\text{NH}_4)_2\text{HPO}_4$  solution at pH 8.15 to 7.40

Original concentration of the solution (molar)	Equilibrium concentration (molar)	Amount of $\text{P}_2\text{O}_5$ adsorbed by 0.5 g. (in g.)
1.00	0.9742	0.0733
0.50	0.4846	0.0435
0.25	0.2418	0.0232
0.20	0.1933	0.0189
0.10	0.0961	0.0111
0.04	0.0383	0.0047
0.02	0.0190	0.0027
0.01	0.0094	0.0015

TABLE No. 8.

Adsorption of phosphate by ilmenite from  $(\text{NH}_4)_2\text{HPO}_4$  solution at pH 8.15 to 7.40

Original concentration of the solution (molar)	Equilibrium concentration (molar)	Amount of $\text{P}_2\text{O}_5$ adsorbed by 0.5 g. (in g.)
1.00	0.9673	0.0916
0.50	0.4817	0.0517
0.25	0.2401	0.0280
0.20	0.1920	0.0227
0.10	0.0949	0.0145
0.04	0.0383	0.0048
0.02	0.0189	0.0029
0.01	0.0093	0.0016

TABLE No. 9.

Adsorption of phosphate by  $\text{TiO}_2$  from  $\text{NH}_4\text{H}_2\text{PO}_4$  solution at pH 8.15 to 7.40

Original concentration of the solution (molar)	Equilibrium concentration (molar)	Amount of $\text{P}_2\text{O}_5$ adsorbed by 0.5 g. (in g.)
1.00	0.9685	0.0892
0.50	0.4814	0.0526
0.25	0.2402	0.0277
0.20	0.1914	0.0241
0.10	0.0952	0.0135
0.04	0.0378	0.0060
0.02	0.0187	0.0035
0.01	0.0093	0.0019

TABLE No. 10.

Adsorption of phosphate by ilmenite from  $\text{NH}_4\text{H}_2\text{PO}_4$  solution at pH 8.15 to 7.40

Original concentration of the solution (molar)	Equilibrium concentration (molar)	Amount of $\text{P}_2\text{O}_5$ adsorbed by 0.5 g. (in g.)
1.00	0.9603	0.1126
0.50	0.4771	0.0641
0.25	0.2371	0.0365
0.20	0.1897	0.0290
0.10	0.0945	0.0154
0.04	0.0378	0.0060
0.02	0.0186	0.0036
0.01	0.0094	0.0020

TABLE No. 11.

Adsorption of phosphate by  $\text{TiO}_2$  from  $\text{H}_3\text{PO}_4$  solution at pH 0.80 to 2.22

Original concentration of the solution (molar)	Equilibrium concentration (molar)	Amount of $\text{P}_2\text{O}_5$ adsorbed by 0.5 g. (in g.)
1.00	0.9613	0.1093
0.50	0.4795	0.0610
0.25	0.2370	0.0340
0.20	0.1900	0.0290
0.10	0.0946	0.0154
0.04	0.0374	0.0074
0.02	0.0185	0.0042
0.01	0.0091	0.0026

TABLE No. 12.

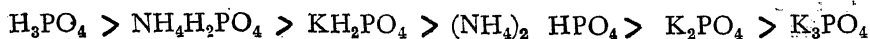
Adsorption of phosphate by ilmenite from  $\text{H}_3\text{PO}_4$  solution at pH 0.80 to 2.22

Original concentration of the solution (molar)	Equilibrium concentration (molar)	Amount of $\text{P}_2\text{O}_5$ adsorbed by 0.5 g (in g.)
1.00	0.9519	0.1364
0.50	0.4737	0.0765
0.25	0.2341	0.0451
0.20	0.1875	0.0355
0.10	0.0915	0.0239
0.04	0.0363	0.0104
0.02	0.0178	0.0060
0.01	0.0087	0.0035

## DISCUSSION

It appears from the experimental results recorded in the foregoing tables (1—12) that the phosphate ions are adsorbed by titanium dioxide and ilmenite, the extent of adsorption depending on the concentration and pH of the solutions. The results indicate that the phosphate adsorption is a function of the concentration of the phosphate solution. The adsorption increases with increase in the concentration of the solution and decreases with decrease in the concentration of the phosphate solution. Thus the adsorption is maximum in molar phosphate solutions and minimum in 0.01 molar solutions.

The pH of the solutions also exert a considerable influence on the adsorption of phosphate. The adsorption is greater at lower pH values than at higher pH values. The  $\text{K}_3\text{PO}_4$  solution which is highly alkaline shows a smaller adsorption of phosphate than phosphoric acid of equivalent concentration which is highly acidic. Thus it is evident that with increase in the acidity of the solution the adsorption increases. The different phosphate solutions can be arranged in the following decreasing order of adsorption.



Moreover ilmenite adsorbs more phosphate than an equivalent amount of titanium dioxide at the same concentration of the phosphate solution. This may be due to the higher adsorption of phosphate by  $\text{Fe}_2\text{O}_3$  present in ilmenite. The adsorption of phosphate by titanium dioxide and ilmenite followed the Freundlich adsorption isotherm.

The comparatively greater adsorption from solutions at lower pH values and especially phosphoric acid may be due to the slight dissolution of titanium dioxide in phosphoric acid and its reprecipitation as titanium phosphate. The amount of  $\text{TiO}_2$  passing in the molar phosphoric acid has been estimated to be 30 p. p. m. Davis<sup>8</sup> has reported that  $\text{FeCl}_3$  and  $\text{AlCl}_3$  added to soil containing  $\text{CaO}$  increased

phosphate fixation especially at low pH values. According to Geilman<sup>9</sup> the amount of  $\text{TiO}_2$  in normal soils varies from 0.36% to 0.6% but may go upto 1%. Joffe and Pugh<sup>10</sup> have reported that  $\text{TiO}_2$  may go upto 1.5%. Also the isoelectric precipitation of titanium phosphate takes place at pH 2.7—2.8. Hence along with iron and aluminium, titanium may also adsorb phosphate especially at low pH values.

The pH measurements carried on with the supernatant liquids after adsorption shows an increase in every case. This indicates the adsorption of H ions as well or release of OH ions in the solution. Fixation of phosphate by the exchange of  $\text{PO}_4$  ions for OH ions have been reported by Mattson<sup>11</sup>, Demolon and Bastisse<sup>12</sup>, Scarseth<sup>13</sup>, Kelley and Midgley<sup>14</sup> and Coleman<sup>15</sup>.

It may be concluded that fixation of phosphate by titanium dioxide and ilmenite in alkaline and acidic solutions is mainly due to adsorption of phosphate ions and precipitation of phosphate occurs only to a very small extent in concentrated acidic solutions. Moreover the ilmenite shows greater adsorption than titanium dioxide.

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# PHOSPHATES IN RELATION TO THE GROWTH OF ALGAE.

By

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The problem of the relation of phosphates to algal growth has been tackled mainly in two ways :—

- (a) by determining the phosphate content of the waters in which the algae are found in the natural condition and
- (b) by varying the amount of phosphate supplied to the medium and noting its effect on the growth of the algae in artificial culture.

The algae that have been studied are mostly minute and are constituents of the phytoplankton.

The phosphate content of the waters of the lakes of both Europe and America is generally low varying from about 0.01 to 0.02 parts per million, and is, therefore, one of the deciding factors for algal productivity. Deevey (1940) obtained a close correlation between total phosphorus content and chlorophyll-content (as a measure for algae) of the lakes in the United States. Oceanographic studies by Harvey (1942) have shown that growth of marine planktonic algae correlates closely with the phosphate content of the water.

Chu (1942) has experimentally studied the effect of different concentrations of phosphate on a number of planktonic algae grown in synthetic media. The phosphate requirements of the algae investigated lay considerably above the concentration usually existing in the lakes. Using  $K_2HPO_4$  with cultures of *Scenedesmus* Osterlind (1949) noted that this alga requires at least 0.5 mg/litre for growth and no inhibition occurs even at 10mg/litre. Under similar cultural conditions Rhode (1948) found 1.12mg/litre is the lowest concentration of phosphate in the basic medium which gives good growth in the green alga *Ankistrodesmus*. Increase of phosphate can give higher yield but other factors become limiting so that all available phosphate is not utilised.

*Utilisation of phosphate*—Utilisation of phosphate depends not only on the nature of the compound but also on the presence of other ions specially nitrates. Ketchum (1939) has studied the interplay of phosphate and nitrate concentrations on the ratio of phosphate/nitrate uptake from seawater by the diatom *Nitzschia*. According to him the ratio of phosphate/nitrate in seawater is 1:20. In artificial cultures the rate of phosphate absorption is dependent on both nitrate and phosphate concentration but the rate of absorption of nitrate is independent of the concentration of phosphate. A tenfold increase in the concentration of phosphate has no influence on the rate of absorption of nitrates and results only in a slight increase in the rate of absorption of phosphate. Different concentrations of nitrate, however, influence the absorption of both nitrate and phosphate. Working with pure cultures of Myxophyceae Gerloff et al (1950 and 1952) noted that maximum growth of *Microcystis* occurs when the P/N ratio is 1/75 while for *Coccochloris* (*Gloeotheca*) it is 1/30.



The amount of dissolved phosphate in the lakes of U. S. A. is only 13% of total phosphorus while 87% is organically bound either in a dissolved or solid state. Similar is the condition in the lakes of other regions. Thus unless organic phosphorus is utilised or broken down, an extremely small amount of phosphate is available to the planktonic algae. Rhode (1948) used various concentrations of adenylic acid prepared from nucleic acid and compared similar concentrations of  $K_2HPO_4$  for the growth of bacteria free cultures of *Scenedesmus* and found that although at the beginning the growth was slow, phosphorus bound in adenylic acid can be utilized although the yields are slightly lower than with corresponding concentrations of  $K_2HPO_4$ . According to Chu (1946) pyrophosphates are not utilized readily as orthophosphates. Under natural conditions organic phosphates are broken down by bacteria but in bacteria-free cultures both phytin and glycerophosphoric acid can be utilized but not lecithin or sodium nucleinate.

Pearsall and Loose (1937) found that the main trends of phosphate utilisation during the growth of *Chlorella* are similar to those occurring during the development of a leaf of the higher plant. Absorption of phosphate always occurs when the cells are grown in light but it is also absorbed in the dark by cells which are deficient in phosphates. Rhode (1948) observed that the same alga after being phosphate-starved when placed in a medium with plentiful supply of phosphate not only covered their shortage within seven days but stored even so much extra phosphate that the growth after being placed again in a phosphate-free medium equalled that in ordinary medium. The alga therefore, accumulated phosphate beyond its immediate need. Ketchum (1939) studied phosphate deficiency in *Chlorella* and *Nitzschia* and found that in phosphate-free media the algae continued to grow until the cells had acquired a 'phosphorus debt' of more than half of the usual content. Addition of phosphate resulted in rapid absorption culminating in restoration of the normal level. The characters of phosphorus deficiency are similar to these of nitrogen deficiency. Carbon assimilation continues in phosphorus deficient cells. Phosphorus deficient cells of *Polytomella* was observed to show accelerated protein synthesis immediately following addition of excess of phosphate to the culture, indicating that inorganic phosphate is immediately available for protein synthesis mechanism.

*Adaptation of algae to phosphate concentration.*—The body of the green algae has a high phosphorus content of about 1 — 1.5% of its dry weight (*Chlorella* — 1.1%) as compared to about 0.2% in higher plants as in *Zea mays* (corn). It is to be expected therefore that green algae would require a high concentration of phosphorus for maximum growth. According to Chu (1943) the lower limit of the optimum range of phosphate concentration for the growth of planktonic green algae (*Pediastrum*, *Staurastrum* etc.) is 0.09 p. p. m. as compared to 0.018 for diatoms. According to Rhode (1948) addition of phosphate at a level of 5  $\mu$ g./litre to the water of a fresh-water lake inhibited the growth of two algae belonging to the Chrysophyceae but addition of nearly 20  $\mu$ g./l was necessary to obtain good growth of the diatom *Asterionella* while 500  $\mu$ g./l was needed for growth of the green alga *Scenedesmus*.

From the above mentioned studies it appears that both qualitative and quantitative phosphate requirements differ with the different groups of algae. Such difference may explain the variations in the composition of the planktonic algae in lakes and other bodies of water. In general the algae may be put in three categories :—

- (a) those with a high phosphorus requirement, being mostly composed of the green algae.

- (b) those requiring a moderate amount of phosphorus i. e. near about 0.02mg./l, consisting mostly of diatoms and
- (c) those having a low phosphorus requirement of much less than 0.02mg./l, comprising the Chrysophyceae and probably the Myxophyceae.

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# PHOSPHATE FIXATION CONTRA PHOSPHATE AVAILABILITY

By

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A great many scientists have devoted considerable time for study of phosphate fixation in soils of various types and under varying conditions. The results have generally been discouraging from the farmers point of view. Of phosphatic fertilizers added to a soil only a small portion of the phosphorus was taken up by the plants, the rest being retained in the soil in such a state that it is more or less unavailable for crop plants. The practical result of these investigations has been the recommendation of large amounts of phosphate fertilizers so that in all events the need of the crop should be covered. In countries on a high industrial level as in western Europe and in U. S. A. sufficient amounts of phosphatic fertilizers may easily be obtained and at such prices so as to make large applications profitable. In more purely agricultural countries the use of such large quantities of phosphate may be prohibitive.

Much less attention has been paid to the problem of holding or making phosphate in an available state in the soil. However, this problem must be the more important one for the greater part of the world.

Already in the early '30s the writer, Åslander (1932) came in contact with the problem of phosphate fixation contra phosphate availability. The leading investigation of that time in this part of the world at least was the one by Gaarder (1930). In solutions of phosphates containing Fe or Al the pH of the solution governed phosphate solubility. In acid solutions the solubility was low or practically nil, Fig. 1 and Fig. 2. The interpretation, of the results, especially by agriculturists, was that the low yields often observed on acid soils were caused by phosphate deficiency owing to phosphate fixation by the soils. Heavy liming in order to change the soil reaction was recommended. Such a liming is expensive for the farmer. Moreover, the writer had observed very good yields of for instance winter wheat, barley and sugar beets on distinctly acid soils, pH 5.0 to pH 5.6, where phosphates in the soil according to Gaarder's (1930) results ought to be more or less unavailable for the plants. The very large yields actually obtained under such conditions demonstrated, however, beyond any doubt that phosphate must be easily available for the plants in spite of the acid soil reactions. Liming is not the only method of facilitating phosphate solubility in the soil. The writer, Åslander (1932), concluded that it seems advisable not to regard the conditions of phosphate solubility demonstrated by Gaarder in pure solutions as being representative of conditions in the soil, especially not in a soil rich in humus. Humus constituents have a great ability to form complexes, for instance with iron. For that reason it is probable that a repetition of Gaarder's investigation in the presence of humus extracts would give quite different values for the solubility of phosphates. This prediction of the influence of humus on the solubility of phosphates was confirmed far beyond expectation. Gaarder and Grahl-Nielsen (1935) continued the investigation of factors governing the solubility of phosphates, and it was found that in the presence of humus extracts phosphates were equally soluble between pH 1 and pH 8, Fig. 3. This result is of the utmost importance from both the scientific and the practical point of view. For instance, it explained the observation of large yields on acid soils, it suggested that an expensive liming is superfluous in connection with the problem of phosphate solubility and also that there is no need of using very large

quantities of phosphate fertilizers. Strange enough, this later result seems to have caught only slight attention. When the pictures in Figs. 1—3 were taken from the papers of Gaarder (1930) and Gaarder and Grahl-Nielsen (1935) in a great library it was found that the first paper was read almost to pieces while the second one was not even cut open.

In pot cultures, Åslander (1932), it was found that when acid soils very poor in plant nutrients by standard fertilization were made as rich as neutral or slightly alkaline the yields of barley were excellent and unaffected by soil reaction in mical soils between p H 5, and p H 8, and in humus soils down to p H 4. Thus, in humus soils phosphate is available under all conditions. Humus can be used to prevent phosphate fixation by soils.

In western Europe dairy farms are the common type. Large amount of farmyard manure are used. The manure is decomposed to humus in the soil and ought for that reason to be a good means for the farmer to prevent phosphate fixation. An early experiment was carried out in the late '30s, Åslander (1940). On an acid soil extremely poor in readily soluble phosphate, superphosphate and other phosphates were added single or thoroughly mixed with farmyard manure, the manure used being especially poor in phosphorus as a result of lean rations. A first crop of barley was overrun by weeds but the second crop of red clover and timothy grass have excellent yields, Fig. 4. Phosphates were available in the soil in spite of the acid reaction on plots where phosphates were mixed with farmyard manure. It was also found that nodules were formed in large quantities on red clover plants on the phosphate-manure plots but not on plots where phosphates were added without manure. Even the nodule bacteria will benefit by the phosphate-manure mixture.

More recently it was possible to study the ability of various forms of humus to prevent phosphate fixation, Åslander (1954). In the laboratory superphosphate, the absolutely dominating phosphate fertilizer of the country, was added to various types of soils and the phosphate fixation determined. The fixation was very high. Thereafter superphosphate was mixed with farmyard manure, Sphagnum peat (used in the cow-houses as an absorbent), compost made up of straw, and green manure, clippings of a lawn. The percentage of phosphate soluble various solvents was determined immediately, after one month and after five months. The results obtained with superphosphate mixed with farmyard manure are recorded in Table 1.

TABLE 1  
Solubility of phosphoric acid in superphosphate mixed with farmyard manure in percentage of amounts added.

Solvents		Time of storage					
		Immediately		After 1 month		After 5 months	
		P	pH	P	pH	P	pH
Mixed acids 1/1	...	100	3.46	90.2	3.51	100	3.54
Mixed acids 1/4	...	100	5.25	92.5	5.54	100	5.66
CO <sub>2</sub> water	...	68.3	5.70	54.8	5.89	47.0	6.28
Water	...	31.2	6.72	19.4	7.00	8.7	7.54

Fig. 1.—The solubility of phosphates in the presence of Fe. (Gaarder 1930).

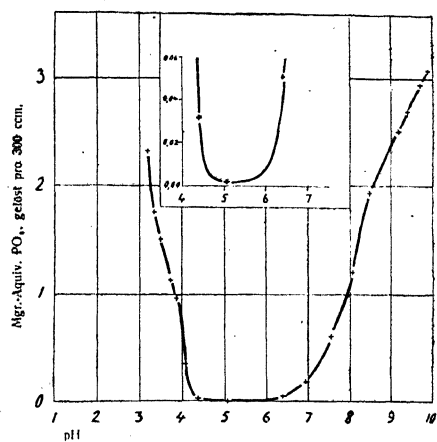
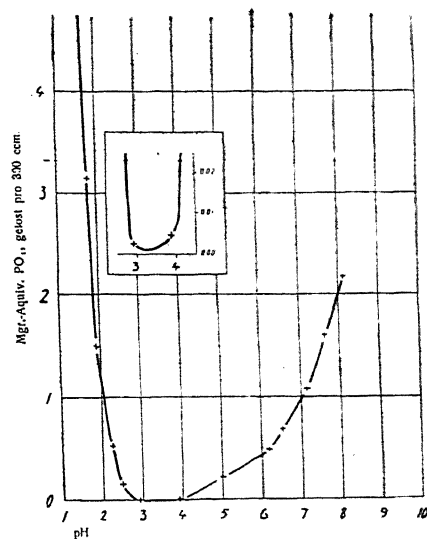


Fig. 2.—The solubility of phosphates in the presence of Al. (Gaarder 1930).

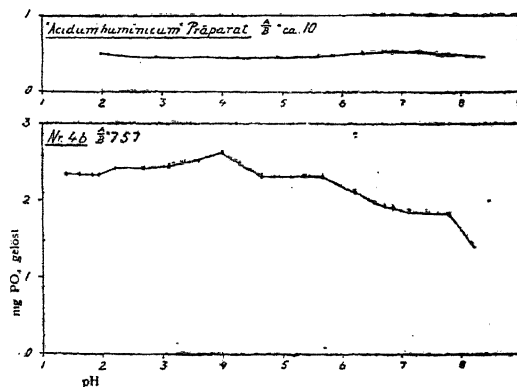


Fig. 3.—The solubility of phosphates in the presence of humus. No influence of pH. (Gaarder and Grahl-Nielsen 1935.)



A

B

Fig. 4. — Before and after phosphate fertilization according to the writer's method on a gytja soil extremely poor in phosphates. A. The crop failure prompted the investigation. B. Red clover growing splendidly at pH 4.5 after phosphate fertilization. (Aslander 1940).

Table 1. DRY MATTER YIELD and PHOSPHORUS UPTAKE OF CORN  
(average of three replicates)

Treatment <sup>1/</sup>	Dry Matter Yield grams / pot			Phosphorus Uptake milligrams / pot		
	0 P <sup>2/</sup>	P sep	P com	0 P	P sep	P com
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	4.79	7.79	8.15	10.35	10.35	12.44
(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	4.40	7.55	5.76	10.13	9.45	9.54
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	5.27	7.64	6.31	6.40	11.05	0.70
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	5.62	8.21	8.01	13.02	11.00	11.99

1/ N added to all at 75 pounds / acre

Oxalate equivalent to 310 pounds H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> / acre

2/ 0 P = soil phosphate level

P sep = 100 pounds P<sub>2</sub>O<sub>5</sub> / acre separate from anion material

P com = 100 " " combined with " "

Table 2. PHOSPHORUS A VALUES and PERCENTAGE OF PHOSPHORUS  
DERIVED FROM SUPERPHOSPHATE TREATMENTS  
(average of three treatments)

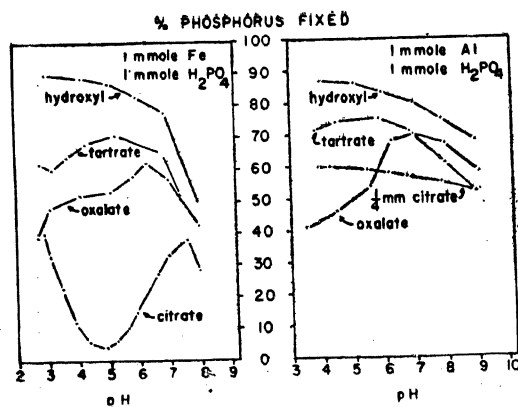
Treatment <sup>1/</sup>	% Plant P Derived From Fertiliser		Phosphorus A Value, pounds P <sub>2</sub> O <sub>5</sub> / acre	
	Separate <sup>2/</sup>	Combined <sup>3/</sup>	Separate	Combined
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	38.0	41.6	165	144
(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	37.7	29.1	165	243
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	36.1	25.8	162	287
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	37.0	23.8	170	318

1/ N added to all at 75 pounds / acre

Oxalate equivalent to 310 pounds H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> / acre

2/ Anion material separate from superphosphate

3/ Anion material combined with superphosphate



In mixed acids (90 per cent lactic acid and 10 per cent HCl, the writer's mixture for determining readily soluble plant nutrients in a soil) the solubility of phosphoric acid is complete. The drop in solubility occurring after storage for one month probably is the evidence of microbacterial activity. The superphosphate added was only one per cent of the manure, so that the quantity actually absorbed was not very large. In CO<sub>2</sub> water the solubility was diminished. The fixation mechanism is probably that the watersoluble monocalciumphosphate in superphosphate is converted into tricalciumphosphate in the dung.

The experiment with compost gave somewhat lower solubility of the phosphate, probably owing to the addition of cyanamid to the straw. In green manure the solubility was very similar to that in farmyard manure.

Several experiments were carried out with superphosphate mixed with humus forming materials and the mixture thereafter mixed with soils of various types. In Table 2 typical results are shown.

TABLE 2

Solubility of phosphoric acid in superphosphate after mixing with humus forming materials in soil No. 4 Lanna in percentage of amounts added.

Mixtures	Solvents							
	1/1 acid		1/4 acid		CO <sub>2</sub> water		Water	
	P	pH	P	pH	P	pH	P	pH
Superphosphate alone.	3.9	3.50	2.8	4.32	2.7	5.28	0.2	5.90
Superphosphate plus:								
Farmyard manure.	17.2	3.42	15.5	1.15	9.6	5.12	8.8	5.70
Sphagnum peat	9.1	3.49	8.4	4.11	4.9	4.85	5.6	5.28
Compost ...	11.8	3.59	3.7	4.35	4.9	5.07	3.6	5.60
Green manure	18.5	3.60	10.8	4.60	8.8	5.80	6.5	6.90

The solubility in the system phosphate-humus-soil is very much lower than in the system phosphate-humus but still considerably higher than in the system phosphate-soil. A phosphate fixation takes place during the extraction process which was continued for 18 hours.

The practical value of the method of mixing phosphate with humus forming materials is much greater than the figures in Table 2 indicates. In the soil, phosphate holding manure is spread in lumps where the phosphate is mechanically protected from the fixing agents of the soil. In field trials it has been found that superphosphate mixed with farmyard manure will satisfy the need of the crops grown for three to four years. In a seven years rotation phosphate plus manure

(or stubble) is added twice only. Considerably less phosphate is needed than generally recommended.

Further investigations are in progress, although on a very limited scale.

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# COMPARATIVE VALUE OF INDIAN ROCK PHOSPHATES AND BASIC SLAGS

By

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Indian deposits of rock phosphate occur in Singhbhum District in Bihar and in Trichinopoly. These deposits contain fairly good amount of  $P_2O_5$  and can be used as fertilizer. Basic slag, which is a byproduct of the steel industry also contains some phosphate, which has not been used as fertilizer in India. The most commonly accepted formula for the phosphate compound in basic slag is the double silicate and phosphate of lime  $(CaO)_2, SiO_2, P_2O_5$ . Recent researches of Dhar and coworkers<sup>1</sup> have shown that these materials can be used profitably for improving soil fertility. The present work has been undertaken to assess the comparative value of Indian rock phosphates and basic slags (obtained from Tata and Kulti factories) with the Algerian rock phosphate and dicalcium phosphate, which is although a sparingly soluble compound but has much to recommend as a soil amendment.

Many methods have been utilized for assessing the availability of various phosphates in soils. The various extraction methods are based upon their (1) water solubility (2) carbon dioxide water solubility (3) solubility in various acids, bases, salts and buffered solutions. We have determined the solubility of the phosphates in solutions of acetic acid, tartaric acid, citric acid and carbonic acid.

## EXPERIMENTAL

The analysis of the rock phosphates and basic slags was carried out according to the procedure described by Washington<sup>2</sup>. Different solutions of acetic, citric, and tartaric acids were prepared ranging in strength from Normal to 0.001N. The phosphatic material was finely powdered and passed through 150 mesh sieve. 1 gm. of the material was shaken with 100ml. of the acid solution in a 250 ml. Jena glass bottle and allowed to stand for 24 hours at 30°. On the next day the supernatant clear liquid was filtered and  $P_2O_5$  estimated in it volumetrically using ammonium molybdate. The same procedure was repeated with solutions of carbonic acid prepared by passing  $CO_2$  in double distilled water for different periods. The concentration of  $CO_2$  in solution was estimated by baryta water.

## Observations:

TABLE I  
Composition of materials used

	Trichinopoly rock phosphate	Algerian rock phosphate	Tata basic slag	Kulti basic slag
Silica	11.2	4.32	23.7	17.7
Sesquioxide	30.6	0.12	20.8	15.9
$Fe_2O_3$	4.4	...	16.8	10.1
CaO	21.3	13.3	34.4	46.5
MgO	1.7	1.9	5.3	6.3
$K_2O$	0.05	8.5	9.1	...
$P_2O_5$	27.8	26.4	7.6	3.8

TABLE 2

Solubility of phosphatic materials in carbonic acid

Concentration of acid in ml of CO <sub>2</sub> per litre	P <sub>2</sub> O <sub>5</sub> soluble in gms./litre				
	Dical phosphate (anhydrous)	Trichi rock phosphate	Algerian rock phosphate	Tata basic slag	Kulti basic slag
...	0.0009	0.0120	0.0131	0.0061	0.0031
44.00	0.2625	0.0140	0.0180	0.0452	0.0110
71.50	0.2847	0.4145	0.0180	0.0458	0.0118
205.30	0.3236	0.0152	0.0185	0.0465	0.0125
378.50	0.3813	0.0158	0.0192	0.0471	0.0148

TABLE 3

Solubility in organic acids: Dicalcium phosphate (anhydrous).

Concentration of acid	%P <sub>2</sub> O <sub>5</sub> Soluble		
	Citric acid	Tartaric acid	Acetic acid
N	all Soluble	all Soluble	27.59
0.1N	42.53	38.33	12.34
0.01N	14.25	10.70	3.72
0.001N	1.57	1.78	1.71

TABLE 4

Trichinopoly rock phosphate

N	28.09	20.25	2.82
0.1N	12.51	8.22	0.73
0.01N	0.85	0.95	0.60
0.001N	0.70	0.82	0.50

TABLE 5  
Algerian rock phosphate

N	32.09	25.77	4.35
0.1N	14.26	8.28	1.85
0.01N	3.82	3.50	0.90
0.001N	1.21	1.09	0.65

TABLE 6  
Tata basic slag

N	92.59	81.55	47.87
0.1N	45.53	40.15	18.52
0.01N	15.72	10.85	1.81
0.001N	1.80	1.40	1.32

TABLE 7  
Kulti basic slag

N	9.53	7.01	4.20
0.1N	6.09	5.83	3.52
0.01N	4.10	3.93	2.15
0.001N	1.25	1.12	1.20

#### DISCUSSION

Table 2 shows the effect of passing  $\text{CO}_2$  in suspensions of dicalcium phosphate, Trichinopoly rock phosphate, Algerian rock phosphate, Tata basic slag and Kulti basic slag. It is evident that even small concentration of  $\text{CO}_2$  is able to decompose the phosphate present in the basic slag to an appreciable extent. The data shows that the  $\text{P}_2\text{O}_5$  solubility of Tata basic slag has increased nearly eight times than in water alone. In the case of Kulti slag the increase in the solubility of  $\text{P}_2\text{O}_5$  is less marked than with Tata basic slag. However, there has been small increase in the  $\text{P}_2\text{O}_5$  solubility of both Trichinopoly and Algerian rock phosphates in carbonic and acid solutions. Thus from the carbonic acid solubility point of view, Tata basic

slag appears to contain more available  $P_2O_5$  than Kulti basic slag, Trichinopoly rock phosphate and Algerian rock phosphate.

The dissolving action of  $CO_2$  water upon these materials can be attributed to the conversion of tricalcium phosphate present in them to more soluble mono and disalts because the second and third dissociation constants of phosphoric acid are smaller than the total dissociation constant of carbonic acid. Thus, the small amount of  $H^+$  ions available from carbonic acid can easily convert  $PO_4^{3-}$  into  $HPO_4^{2-}$  and  $H_2PO_4^-$  ions.

If we assume that the amount of  $P_2O_5$  in solution is the measure of the usefulness of these materials, then their comparative value may be represented according to the following order:

Dicalcium phosphate > Tata basic slag > Algerian rock phosphate > Trichinopoly rock phosphate > Kulti basic slag.

Tables (3—6) show the effect of citric, tartaric and acetic acids upon the solubility of these materials. From a close study of the data it appears that Kulti basic slag is very slightly soluble in these acids. However, in comparison to Kulti slag and the rock phosphates, the Tata basic slag is highly soluble in all the three acids. The results further show that Tata basic slag, Trichinopoly rock phosphate and Algerian rock phosphates are dissolved in greater amounts in solutions of citric and tartaric acids than in acetic acid. The dissolving action of these acids may be partially ascribed due to hydrogen ions and also due to the formation of soluble complexes by the anions of these acids with the phosphate present in these materials. It is of interest to record here that experimental evidence has been obtained supporting the view that the addition and decomposition of certain plant residues or manures provides certain organic anions which react with iron and aluminium phosphates to form complexes (Swenson et.al,<sup>3</sup> Struthers and Sieling,<sup>4</sup> Dalton et.al<sup>5</sup>).

These organic acid solubility tests also show that Tata basic slag can serve as a better phosphatic fertilizer than the Trichinopoly rock phosphate, Algerian rock phosphate or Kulti basic slag. These results are in accordance with those obtained by Dhar and coworkers<sup>1</sup>, when the addition of Tata basic slag with decomposing organic matter increased the available phosphate status of soils markedly.

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# INFLUENCE OF SOME SALTS UPON THE $P_2O_5$ SOLUBILITY OF SPARINGLY SOLUBLE PHOSPHATES

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The phase of phosphate research dealing with the reaction of salts on sparingly soluble phosphates, as they affect the phosphate solubility in soils has become increasingly important during recent years. Moreover, with the increasing use of phosphatic fertilizers and consequently with a corresponding accumulation of residual phosphate in soils, it is necessary that a systematic study of the influence of salts upon the solubility of different phosphates should be carried on, in order to clarify most of the conflicting data recorded in literature.

Wild<sup>1</sup>, has summarised the studies on the effect of salts on phosphate solubility and concluded that there is insufficient knowledge to explain the apparently contradictory results. Cameron and Hurst<sup>2</sup>, observed that KCl and  $NaNO_3$  have a solvent action upon the phosphate of calcium. Heiden<sup>3</sup>, reported that sodium, potassium and ammonium salts increase the solubility of ferric phosphate but in some cases it decreases. Karlsson and Mattson<sup>4</sup> found that N/2 KCl solution increased the solubility of powdered apatite twofold. Norman and Pierre<sup>5</sup> have reported that the solvent action of the neutral salts is due to 'salt effect' based on the theory of Lewis and Randall, according to which, the activity coefficients of the ions of the sparingly soluble phosphate decrease resulting in the increase in the solubility of the phosphate. It seems that this mechanism may not be applicable in the case of sparingly soluble phosphates, because these phosphates hydrolyse immediately as soon as they come in contact with water and that their solubility is mainly due to hydrolysis. There is always more  $P_2O_5$  in solution than the basic part in comparison to the ratio in which they are present in the original solid. In order to explain the effects of KCl on phosphate solubility, a view point has been advanced that KCl may enter into a specific reaction with the phosphate.

In view of the contradictory observations, regarding the solubility of phosphates in salts, an attempt has been made to determine the solubility of aluminium phosphate, ferric phosphate, dicalcium phosphate, tricalcium phosphate, dimagnesium phosphate and trimagnesium phosphate in solutions of KCl, NaCl,  $NH_4Cl$ ,  $KNO_3$ ,  $NaNO_3$  and  $NH_4NO_3$ .

## EXPERIMENTAL

1 gm of the phosphate was shaken with 100 ml of M/10 salt solutions mentioned above in a 250 ml Jena glass bottle, in a mechanical shaker for one hour. The bottles were allowed to stand for 24 hours at 30°. On the next day the clear liquid was filtered through a sintered funnel attached to a filtration flask and suction pump. Aliquot portions were taken for the estimation of  $P_2O_5$  volumetrically using ammonium molybdate. The pH of the solutions was also determined. The experiment were carried on under similar conditions and with as much uniformity as possible, so that the errors in solubility due to variation in time of contact of the phosphate and the solution may be minimised.

Observations:

TABLE 1

100ml of M/10		$P_2O_5$ (gms./litre)	pH	$P_2O_5$ (gms./litre)	pH
Salt solution		Aluminium phosphate		Ferric phosphate	
H <sub>2</sub> O only	...	0.0974	7.55	0.0449	6.80
KCl	...	0.0648	7.34	0.0358	6.52
NaCl	...	0.0625	7.35	0.0340	6.55
NH <sub>4</sub> Cl	...	0.0593	7.40	0.0324	6.60
KNO <sub>3</sub>	...	0.0578	7.30	0.0114	6.20
Na NO <sub>3</sub>	...	0.0540	7.35	0.0110	6.25
NH <sub>4</sub> NO <sub>3</sub>	...	0.0505	7.40	0.0102	6.30

TABLE 2

		Tricalcium phosphate		Dicalcium phosphate (anhydrous)	
H <sub>2</sub> O only	...	0.1293	5.70	0.0509	7.50
KCl	...	0.4963	5.60	0.0872	7.30
NaCl	...	0.5531	5.55	0.0566	7.25
NH <sub>4</sub> Cl	...	0.5877	5.50	0.1050	7.20
KNO <sub>3</sub>	...	0.5978	5.50	0.0968	7.25
NaNO <sub>3</sub>	...	0.6882	5.48	0.0911	7.18
NH <sub>4</sub> NO <sub>3</sub>	...	0.7260	5.45	0.1095	7.10

TABLE 3

		Trimagnesium phosphate		Dimagnesium phosphate (trihydrate)	
H <sub>2</sub> O only	...	0.2800	7.40	0.4250	7.52
KCl	...	0.4098	7.28	0.5770	7.40
NaCl	...	0.4831	7.25	0.6615	7.35
NH <sub>4</sub> Cl	...	0.5677	7.20	0.6923	7.35
KNO <sub>3</sub>	...	0.4882	7.10	0.6155	7.32
NaNO <sub>3</sub>	...	0.5935	6.90	0.6727	7.30
NH <sub>4</sub> NO <sub>3</sub>	...	0.6258	6.80	0.7532	7.20

## DISCUSSION

The results recorded in table No. 1 clearly show that salts such as KCl, NaCl,  $\text{NH}_4\text{Cl}$ ,  $\text{KNO}_3$ ,  $\text{NaNO}_3$  and  $\text{NH}_4\text{NO}_3$  decrease the  $\text{P}_2\text{O}_5$  solubility of aluminium and ferric phosphates. On treating these phosphates with the chlorides and nitrates of potassium, sodium and ammonium, it has been observed that the solubility decreases more with the nitrates than with the chlorides. From a close study of the data, it appears, that besides the anions  $\text{Cl}^-$  and  $\text{NO}_3^-$ , the solubility changes with the change of cations also. The maximum depressing effect of cations has been observed with  $\text{NH}_4^+$  and minimum with  $\text{K}^+$ . Thus the depressing effect of these salts upon the solubility of aluminium and ferric phosphates may be represented in the following decreasing order:—

- (i)  $\text{NO}_3^- > \text{Cl}^-$  in the case of anions  
and (ii)  $\text{NH}_4^+ > \text{Na}^+ > \text{K}^+$  in the case of cations.

The results further show that the pH of the resulting salt solutions after mixing with aluminium and ferric phosphates decreases in every case. It is probable that the cations of these salts interact with the phosphates in such a way that selective adsorption of the cations on the surface of the phosphate takes place, so that the anions of the salt are free in solution which account for the decrease in pH. Moreover, this process may produce more insoluble and less hydrolysed phosphates due to which the solubility of the ferric and aluminium phosphates decreases. It is interesting to record in this connection that Hazeman<sup>6</sup> while studying the reaction of phosphate minerals with salts, identified some compounds as members of an isomorphous series belonging to  $(\text{H}, \text{Na}, \text{K}, \text{NH}_4)_3(\text{Fe}, \text{Al})_2\text{PO}_4 \cdot n\text{H}_2\text{O}$ . The decreased solubility and increased fixation of phosphate observed by Ericksson<sup>7</sup> in pot tests with soils rich in sesquioxides and treated with KCl also appears to be due to the fact that the materials resulting from the combination of phosphates and sesquioxides due to fixation, are rendered less soluble by KCl.

The influence of aforesaid salts upon the di and triphosphates of calcium and magnesium is different from the action upon aluminium and ferric phosphates. The concentration of  $\text{P}_2\text{O}_5$  has been observed to increase when the phosphates of calcium and magnesium are treated with these salt solutions. The slight decrease in pH values of the solution is probably due to the fact that more  $\text{P}_2\text{O}_5$  is passing into solution than in water alone. A survey of tables 2 and 3 show that the solubility of calcium and magnesium phosphates is greater in nitrates than in chlorides. On the other hand, the ammonium salts increase the solubility to a greater extent than the sodium or potassium salts. The marked increase of solubility of the phosphates of calcium and magnesium in ammonium salt solutions is likely to be due to the presence of  $\text{H}^+$  ions obtained from the hydrolysis of the ammonium salts which are feebly acidic. Thus the greater solubility of the calcium and magnesium phosphates in presence of different cations and anions can be arranged in the following decreasing order:—

- (a)  $\text{NO}_3^- > \text{Cl}^-$  in the case of anions  
and (b)  $\text{NH}_4^+ > \text{Na}^+ > \text{K}^+$  in the case of cations.

From the foregoing considerations, it can be concluded that when phosphatic fertilizers are added to soils and particularly to saline soils, it is probable that the solubility of the fixed phosphates may be modified. In such soils the conversion of the added phosphate fertilizer to an almost completely unavailable condition due to 'Fixation' seems to be an exaggeration, because in course of time, the phosphates are

rendered available to the plants by the action of neutral salts present in the soil. Evidence has accumulated in recent years (Volk<sup>8</sup>, Enslinger and Cope<sup>9</sup>) that the portion of the phosphate not recovered by the first crop has a definite residual effect. It is probable that besides the phenomenon of hydrolysis, the neutral salts also play an important role in the recovery of the phosphate by the plants.

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# INVESTIGATIONS IN ALUMINIUM AND OTHER SPARINGLY SOLUBLE PHOSPHATES, ROCK PHOSPHATES AND BASIC SLAGS

By

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A very large amount of research work has been carried on regarding the decomposition of sparingly soluble phosphates, finely divided rock phosphates, and basic slag by water, carbonic acid and weak organic acids. The neutralization of phosphoric acid solutions by different sparingly soluble bases and a suitable method of preparing dicalcium phosphate have been studied. In this paper some of our results and conclusions are recorded.

When sparingly soluble phosphates, viz., aluminium phosphate, ferric phosphate, tricalcium phosphate, dicalcium phosphate (anhydrous), trimagnesium phosphate, dimagnesium phosphate (trihydrate), are suspended in water at 30°, they are hydrolysed into free phosphoric acid in solution and leave a more basic phosphate in the solid residue. The electrical conductivity of these suspensions has been observed to increase and the pH to decrease even upto 900 days, and hence it seems that the hydrolysis reaction continues for a long time. A similar behaviour has been observed for ferrous phosphate, which has only been studied for 300 days at 30°. In the case of Indian basic slags and Algerian rock phosphates, both conductivity and pH increase with lapse of time, but after about 45 days both the values decrease slightly upto 300 days.

As 50° the hydrolysis reaction is intensified. Except for aluminium and tricalcium phosphates, which attain their approximately constant values of electric conductivity and pH after about 30 and 10 days respectively, the hydrolysis reaction with all the other phosphates has been observed to continue even upto 300 days. However, monocalcium phosphate which seems to be decomposed immediately to dicalcium phosphate and phosphoric acid in presence of water changes very little both at 30° and 50°. The neutralization of magnesia and phosphoric acid has been observed to be more complete than the neutralization of lime and phosphoric acid.

When lime is added to dilute solution of phosphoric acid in the  $\text{CaO} : \text{P}_2\text{O}_5$  ratio of 1 : 1, monocalcium phosphate is formed in solution. But when concentrated solutions of phosphoric acid are taken, viz., 2M and 5M, a solid residue of anhydrous dicalcium phosphate is obtained. When lime is added to phosphoric acid in the  $\text{CaO} : \text{P}_2\text{O}_5$  ratio of 2 : 1 dicalcium phosphate is obtained in the solid state. With the variation in the concentration of acid, the degree of hydration of the dicalcium phosphate formed also changes. In these neutralizations, compounds having the composition  $\text{CaHPO}_4 \cdot \text{H}_2\text{O}$  and  $\text{CaHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  have been identified by chemical analysis. With strong phosphoric acid solutions the anhydrous form  $\text{CaHPO}_4$  is invariably formed.

Within the range of phosphoric acid concentrations studied, the maximum yield of dicalcium phosphate has been obtained with 0.5M phosphoric acid when

the molecular ratio of  $\text{CaO} : \text{P}_2\text{O}_5$  is 2 : 1. This may serve as a cheap method of production of dicalcium phosphate for fertilizer and feeding purposes.

Monomagnesium phosphate is formed in solution with all the concentrations of  $\text{H}_3\text{PO}_4$ , when magnesia is added in the  $\text{MgO} : \text{P}_2\text{O}_5$  ratio of 1 : 1. Only dimagnesium phosphate trihydrate is formed in the solid state when magnesia is added in the  $\text{MgO} : \text{P}_2\text{O}_5$  ratio of 2 : 1. Mixtures of di and tri phosphates are formed in the solid state when lime and magnesia are added in the oxide :  $\text{P}_2\text{O}_5$  ratio of 3 : 1 to solutions of phosphoric acid.

Freshly precipitated and air dried hydrous oxide of aluminium has been observed to be more reactive with phosphoric acid than the hydrous oxide of iron. The conductivity and pH measurements further show that more H ions are adsorbed on the surface of the solid in the system hydrous  $\text{Al}_2\text{O}_3 - \text{H}_3\text{PO}_4$  than in hydrous  $\text{Fe}_2\text{O}_3 - \text{H}_3\text{PO}_4$  system. The actual measurements indicate that more  $\text{P}_2\text{O}_5$  is removed from phosphoric acid of the same concentration by hydrous  $\text{Al}_2\text{O}_3$  than by hydrous  $\text{Fe}_2\text{O}_3$ .

When freshly precipitated and air dried hydrous oxides of iron and aluminium are added to phosphoric acid of different concentrations, it is observed that appreciable amounts of iron and aluminium are dissolved. In all the solutions, the amount of aluminium passing into solution is greater than the amount of iron in phosphoric acid of same concentration.

In no case a normal phosphate  $\text{FePO}_4$  has been obtained by the interaction of freshly precipitated and air dried hydrous iron oxide and phosphoric acid from concentrations 0.04M to 2M in the  $\text{Fe}_2\text{O}_3 : \text{P}_2\text{O}_5$  ratio of 1 : 1, 2 : 1 and 3 : 1, but basic phosphates having a greater percentage of  $\text{Fe}_2\text{O}_3$  than in the normal  $\text{FePO}_4$  are formed.

A compound having the composition  $\text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$  or  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$  has been observed to form in the solid state when freshly precipitated and air dried hydrous  $\text{Al}_2\text{O}_3$  is added to 2M phosphoric acid in the  $\text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5$  ratio of 1 : 1. In all the other cases basic phosphates containing greater percentage of  $\text{Al}_2\text{O}_3$  than in normal  $\text{AlPO}_4$  have been observed to form, just as in the case of hydrous iron oxide.

Investigations on the washing of various sparingly soluble phosphates show that the decreasing order of water solubility in the first extract is :—

dimagnesium phosphate > trimagnesium phosphate > tricalcium phosphate > aluminium phosphate > dicalcium phosphate > ferric phosphate > ferrous phosphate > Algerian rock phosphate > Trichinopoly rock phosphate > Tata basic slag > Kulti basic slag.

The decreasing order of water solubility in the tenth water extract is :—

Trimagnesium phosphate > dimagnesium phosphate > aluminium phosphate > tricalcium phosphate > dicalcium phosphate > ferric phosphate > ferrous phosphate > Algerian rock phosphate > Trichinopoly rock phosphate > Tata basic slag > Kulti basic slag.

The results further show that the  $\text{P}_2\text{O}_5$  concentration in the various extracts of trimagnesium, dimagnesium and tricalcium phosphate falls off rapidly in the course of extractions and the residue is left which is a more basic compound than the original material.

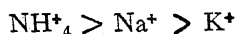
Considerable amounts of  $\text{CaO}$  and  $\text{MgO}$  are also obtained in solutions by washing the various phosphates with water. Calcium carbonate and calcium oxide have been observed to depress the solubility of calcium phosphates, magnesium

phosphates, basic slags, and rock phosphates, but increase the solubility of iron and aluminium phosphates.

Oxides such as  $\text{MgO}$ ,  $\text{ZnO}$  also depress the solubility of these phosphates. The depressing effect of  $\text{MgO}$  is greater than that of  $\text{ZnO}$ .  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  depress the solubility of phosphates to a very small extent and  $\text{TiO}_2$  affects negligibly. It appears that the phenomenon is controlled by the basicity and the solubility products of the hydroxide of calcium, magnesium, aluminium and iron.

Salts such as  $\text{KCl}$ ,  $\text{NaCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{KNO}_3$ ,  $\text{NaNO}_3$  and  $\text{NH}_4\text{NO}_3$  have been observed to modify the solubility of the sparingly soluble phosphates. The solubility of aluminium and iron phosphates decreases by the presence of these salts whereas it increases in the case of other phosphates. The pH of the mixtures increases in the case of rock phosphates and basic slags and decreases slightly in the case of other phosphates. The tri salts are decomposed to a greater extent than the disalts.

It is observed that the solubility of the phosphates is modified both by the change of anions as well as by cations. The depressing effect in the case of aluminium and iron phosphates is greater with nitrate than with chloride. The cations depress the solubility in the following decreasing order:—



A similar order has been obtained in the case of other phosphates which are observed to decompose in presence of salts.

The solubility of aluminium and ferric phosphates has been observed to decrease in presence of carbonic acid whereas the solubility of calcium and magnesium phosphates increases. Basic slags and rock phosphates have also been observed to produce greater amounts of  $\text{P}_2\text{O}_5$  in solutions of carbonic acid than with water alone. The decomposition has been greatest in the case of dicalcium phosphate. The results show that the Tata basic slag is a better phosphatic fertilizer than the Kulti basic slag or the Trichinopoly rock phosphate.

The solubility of the various phosphates has been observed to increase in presence of acetic, tartaric, and citric acids. With the decrease of pH greater amount of phosphate is dissolved. The phosphates of aluminium and iron are comparatively less soluble in these acids than the phosphates of calcium and magnesium. Tata basic slag dissolves to a greater extent than the Kulti basic slag, Trichinopoly rock phosphates or Algerian rock phosphates, which further proves that it is a better phosphatic fertilizer than the Trichinopoly rock phosphate. The dissolving action of the weak organic acids upon the sparingly soluble phosphates has been attributed partly due to  $\text{H}^+$  ions and partly due to formation of the complex organic anions with iron and aluminium. The observations show that the organic anions affect the solubility of the phosphates in the following decreasing order:—



The solubility of the various phosphates in alkali solutions is maximum with  $\text{NaOH}$ , less with sodium carbonate and least with sodium bicarbonate. It appears that the decomposition is controlled by the solubility products of the hydroxides of the various metals. Aluminium and iron phosphates have been observed to decompose nearly completely in solutions of  $\text{NaOH}$ . The phosphates of calcium and magnesium are also appreciably decomposed by alkali solutions, but to a less extent than the phosphates of iron and aluminium.

# STUDIES IN LIME-PHOSPHORIC ACID AND MAGNESIA PHOSPHORIC ACID NEUTRALIZATIONS

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The products formed by the interaction of phosphoric acid and lime are complex, because under certain conditions of concentration and temperature, mono, di, tri, phosphates or hydrates or their mixtures may be formed as solid phases in contact with the solution. A large number phosphates of lime with phosphoric acid have been recorded, some of which have not been confirmed. Cameron, Seidell and Bell<sup>1</sup> suggested that the phosphatic compounds are members of a series of solid solutions of phosphoric acid in lime, the limiting solutions of the series being pure calcium hydroxide at one end and a solid solution very close in composition to dicalcium phosphate at the other end. Jolibois<sup>2</sup> obtained the  $\text{CaO}:\text{P}_2\text{O}_5$  ratio in the resulting solid equal to 2.84, 3.43, 3.45 and 4.30 by mixing equal volumes of phosphoric acid and lime in solution. These observations remained unexplained for sometime, until Lorah<sup>3</sup> pointed out that this ratio was due to adsorption of  $\text{Ca}(\text{OH})_2$  on tricalcium phosphate.

The electrometric titration of calcium hydroxide with phosphoric acid has been studied by Hoffman and Gorter<sup>4</sup>, Täufel and Wagner<sup>5</sup> and Britton.<sup>6</sup> Sanfourche studied the reaction of calcium hydroxide and phosphoric acid at  $100^\circ\text{C}$  and observed that a tribasic phosphate, hydroxy apatite and a mixture of tetrabasic phosphate and hydroxy apatite had been formed. He regarded the tri and tetra basic phosphates to be salts of acid  $\text{H}_3\text{P}_2\text{O}_9$ .

Belopol'skii<sup>8</sup> and coworkers studied the formation of magnesium phosphates within a range of  $\text{P}_2\text{O}_5$  concentration from 0.05 to 70.0%. From their researches they concluded that at  $25^\circ$  within these concentration limits, the solubility isotherm comprises of the saturation branches of:  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ ;  $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ;  $\text{Mg}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Mg}(\text{H}_2\text{PO}_4)_2$ . The liquid phases in the line of saturation with dimagnesium phosphate consist of solutions of the latter in phosphoric acid.

## EXPERIMENTAL

35 ml of standard solutions of phosphoric acid of concentrations 5M, 2M, M, 0.5M, 0.2M, 0.1M and 0.04M were taken in 250 ml Jena glass bottles and equivalent amounts of previously dried  $\text{CaO}$  and  $\text{MgO}$ , in the oxide:  $\text{P}_2\text{O}_5$  ratio of 1:1, 2:1 and 3:1 were weighed. The oxides were then added in the respective bottles with constant shaking. After the oxide had been completely added, the bottles were shaken in a mechanical shaker for one hour and then left over for 24 hours in a bath at  $30^\circ$ . On the next day the solid was drained by suction in a sintered crucible. The solid was rapidly washed first with pure acetone and then with ether. It was thoroughly dried by suction and was analysed for the  $\text{P}_2\text{O}_5$  content and the basic constituents.

**Observations:**
*Analysis of the residues*

Conc. of $\text{H}_3\text{PO}_4$	Molar Ratio of oxide: $\text{P}_2\text{O}_5$	Nature of residuc	
		Lime-phosphoric acid system	Magnesia-phosphoric acid system
0.04M	1:1	No residuc	No residuc
	2:1	$\text{CaHPO}_4 \cdot \text{H}_2\text{O}$	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$
	3:1	2.7 $\text{CaO} : \text{P}_2\text{O}_5$	2.7 $\text{MgO} : \text{P}_2\text{O}_5$
0.1M	1:1	No residuc	No residuc
	2:1	$\text{CaHPO}_4 \cdot \text{H}_2\text{O}$	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$
	3:1	2.6 $\text{CaO} : \text{P}_2\text{O}_5$	2.9 $\text{MgO} : \text{P}_2\text{O}_5$
0.2M	1:1	No residuc	No residuc
	2:1	$\text{CaHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$
	3:1	2.8 $\text{CaO} : \text{P}_2\text{O}_5$	2.7 $\text{MgO} : \text{P}_2\text{O}_5$
0.5M	1:1	No residuc	No residuc
	2:1	$\text{CaHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$
	3:1	2.7 $\text{CaO} : \text{P}_2\text{O}_5$	2.8 $\text{MgO} : \text{P}_2\text{O}_5$
M	1:1	No residuc	No residuc
	2:1	$\text{CaHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$
	3:1	2.8 $\text{CaO} : \text{P}_2\text{O}_5$	2.7 $\text{MgO} : \text{P}_2\text{O}_5$
2M	1:1	$\text{CaHPO}_4$	No residuc
	2:1	$\text{CaHPO}_4$	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$
	3:1	2.6 $\text{CaO} : \text{P}_2\text{O}_5$	2.8 $\text{MgO} : \text{P}_2\text{O}_5$
5M	1:1	$\text{CaHPO}_4$	No residuc
	2:1	$\text{CaHPO}_4$	$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$
	3:1	2.5 $\text{CaO} : \text{P}_2\text{O}_5$	2.8 $\text{MgO} : \text{P}_2\text{O}_5$

**DISCUSSION**

Dicalcium phosphate which is manufactured by the addition of lime to phosphoric acid, as reported by Waggaman<sup>9</sup> is not pure. The product thus formed is contaminated with the triphosphate. There exists a great doubt in the minds of chemists, as to whether or not tricalcium phosphate is actually the final product of complete neutralization of phosphoric acid and lime, when neutralization of phosphoric acid by lime takes place in the  $\text{CaO} : \text{P}_2\text{O}_5$  ratio of 3:1.

It would naturally be expected that the successive addition of 1.2 and 3 moles of CaO to a mole of  $P_2O_5$  in the form of phosphoric acid would result in the formation of mono, di and tri salts of phosphoric acid, but from the results recorded previously, it appears that a different state of affairs exists in the system. On mixing lime and phosphoric acid in the CaO:  $P_2O_5$  ratio of 1:1, it has been observed that the whole of CaO has dissolved in phosphoric acid from concentrations 0.04 M to M and the solution was observed to be acidic. This is due to formation of monocalcium phosphate in solution. With 2M and 5M acids the whole of CaO does not dissolve and a solid residue remains which has the composition of anhydrous dicalcium phosphate  $CaHPO_4$ . This peculiar behaviour is due to the fact that first monocalcium phosphate may be formed, but in very concentrated solutions, it breaks up into dicalcium phosphate and free phosphoric acid. This is a remarkable observation that in concentrated solutions of phosphoric acid, when lime is added in the CaO:  $P_2O_5$  ratio of 1:1, a solid residue having CaO:  $P_2O_5$  ratio of 2:1 for dicalcium phosphate has been obtained instead of monocalcium phosphate.

When lime and phosphoric acid are mixed in CaO:  $P_2O_5$  ratio of 2:1 the resulting solid has been found to be dicalcium phosphate but from a study of their percentage composition it appears that these dicalcium phosphates are associated with different amounts of water. At the acid concentrations of 0.04M and 0.1M, a solid resembling in composition to  $CaHPO_4 \cdot H_2O$  is formed. With 0.2M, 0.5M and Molar acids the solid is very close in composition to  $CaHPO_4 \cdot \frac{1}{2}H_2O$ . At higher acid concentrations of 2M and 5 M the solid formed appears to be  $CaHPO_4$ . It seems that as the acid concentration is increased, the solid formed has a tendency to pass on from the hydrated to the anhydrous form of dicalcium phosphate due to the heat of the reaction and weaker attraction of phosphoric acid.

In the mixture in which lime is added to phosphoric acid in the CaO:  $P_2O_5$  ratio of 3:1, it has been observed that neither pure dicalcium phosphate nor tricalcium phosphate is formed in the solid state, but a mixture of the two is formed. The ratios of CaO:  $P_2O_5$  in the solids formed in the different acid concentrations are 2.72, 2.57, 2.79, 2.69, 2.80, 2.59 and 2.54 respectively. From the foregoing considerations, it is evident that the neutralization of phosphoric acid with lime, in the CaO:  $P_2O_5$  ratio of 3:1, the transformation of lime into tricalcium phosphate is incomplete.

The great utility of dicalcium phosphate as a phosphatic fertilizer and animal feeding material has now been established. Its wide use is hampered by the fact that its cost of production is higher than that of superphosphate. Thus the cheap production of this material needs a careful consideration. The results presented in the foregoing pages clearly indicate that it can be conveniently prepared by adding lime to phosphoric acid in the CaO:  $P_2O_5$  ratio of 2:1. It can also be prepared by taking phosphoric acid of concentration 2M or higher and adding lime to it even in the CaO:  $P_2O_5$  ratio of 1:1. The first method will prove cheaper than the second.

One main difference which has been observed in the mode of formation of the two groups of phosphates when the oxides of calcium and magnesium are added to different concentrations of phosphoric acid, is that in the case of magnesium when the molecular ratio of  $MgO:P_2O_5$  is 1:1, then in every case the solid remains dissolved completely. In this case no solid residue is obtained even with concentrated solutions. This behaviour may probably be due to the fact that monomagnesium phosphate is more stable at higher concentrations, than the monocalcium phosphate which easily decomposes to dicalcium phosphate and phosphoric acid under similar conditions, whereas the monomagnesium phosphate does not decompose to produce

solid dimagnesium phosphate. Another difference which is evident from our data, is that when magnesia and phosphoric acid are mixed in the  $\text{MgO:P}_2\text{O}_5$  ratio of 2:1, then all the acid concentrations from 0.04 M to 5M, a solid residue corresponding to the composition of dimagnesium phosphate trihydrate has been formed whereas in the lime-phosphoric acid system, dicalcium phosphates were formed with different degrees of hydration. The solids obtained when magnesia and phosphoric acid are mixed in the  $\text{MgO:P}_2\text{O}_5$  ratio of 3:1, do not exhibit a definite  $\text{MgO:P}_2\text{O}_5$  ratio. It appears that mixtures of di and tri phosphates of magnesium are formed as the ratios of MgO and  $\text{P}_2\text{O}_5$  in these residues are 2.73, 2.88, 2.73, 2.80, 2.70, 2.80 and 2.84. This behaviour is common both in the calcium and magnesium oxide systems.

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# STUDIES IN PHOSPHORYLATION

By

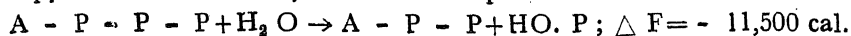
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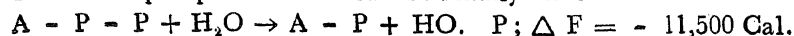
Read at the Silver Jubilee Session of the Academy held at the University of Lucknow on 28th December 1955

In literature dealing with metabolism of carbohydrates and fermentation processes, the formation of phosphorylated carbohydrates, which are believed to be the primary stage in biological reactions has been postulated. Moreover, purine bodies like adenine and adenosine etc. are believed to be forming complexes with different phosphoric acids. These complexes can liberate energy on dephosphorylation. The energy liberation depends on the nature of the phosphorylated compounds formed and their dephosphorylation.

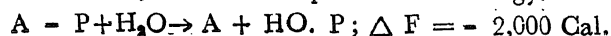
Thus, for example, the terminal phosphate radical of adenosine triphosphate (A T P) can readily be removed by hydrolysis, either by dilute mineral acid or by an enzyme and the process is attended by the liberation of 12,000 Cal. of heat of which 11,500 Cal. correspond to free energy and the remainder to an increase of entropy. The reaction may therefore be represented as follows:



The second phosphate radical can be readily removed:



The third phosphate radical can also be removed by hydrolysis but with much more difficulty and this time only some 2,000 - 3,000 Cal of heat are evolved, of which about 2,000 Cal correspond to free energy.



The yield of free energy in this last reaction is of the same order of magnitude as that found in the hydrolysis of most simple phosphate esters as the glucose phosphates ( $\Delta F = -3,000$  to  $4,000$  Cal) and phosphoglycerol ( $\Delta F = -2,200$  Cal)

Clearly there is some farreaching differences between the bonds by which the first two phosphate radicals are attached and that which binds the third; infact there exist in the A T P molecule two specimens of what may be called "High Energy" or "Energy rich" phosphate bonds as distinct from the third "Energy poor" or "Low energy" phosphate bond which resemble those found in most common phosphate esters. Thus, if we use the special symbol  $\sim$  to represent an energy rich bond, the A T P can be more adequately represented thus:  $A - P \sim P \sim P$ .

Another interesting example of phosphorylation and the energy liberation on dephosphorylation is the fact of "Oxygen debt". During very intense work and activity men and animals may expend 100 times the energy liberated at rest, whereas the consumption of oxygen cannot be increased proportionately. Under such conditions the animal is said to go in for oxygen debt. "Oxygen debt" is associated with increase in concentrations of lactic and phosphoric acids (and perhaps pyruvic acid) and also with a decrease in concentration of phosphocreatine and adenosine pyrophosphate. The "recovery" (at rest) phase is associated with a reverse process, decrease in concentration of lactic and phosphoric acids and increase in concentration of phosphocreatine and adenosine pyrophosphate. It thus appears that when aerobic oxidation is inadequate the energy is obtained by the breaking up of phosphocreatine. During recovery phosphocreatine is



resynthesised at the expense of another energy source. Lohman discovered that adenylyl pyrophosphate is the phosphate carrier; it furnishes the phosphate for the phosphorylation of the creatine as indicated by the reaction; Adenylyl pyrophosphate + creatine  $\rightarrow$  creatine phosphate + adenylic acid. The energy for resynthesis of the phosphocreatine may also come from the oxidation of glycogen to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .  $\text{H}_3\text{PO}_4 + \text{Creatine} + \text{glycogen} + \text{O}_2 \rightarrow \text{phosphocreatine} + \text{CO}_2 + \text{H}_2\text{O}$ .

From a large number of experiments carried out in the Allahabad University Chemical Laboratory and the Sheila Dhar Institute of Soil Science on nitrogen fixation and nitrogen loss, it has been established that stable phosphoproteins are likely to be formed when proteins, amino acids etc. exist or are formed by nitrogen fixation in presence of phosphate, the organic substances undergo slow oxidation in air when mixed with phosphate.

With a view to finding out physico-chemical evidences regarding phosphorylation, we have been carrying on experiments on a group of physical properties such as (a) Molecular Volume (b) Viscosity (c) Molecular lowering of freezing point, (d) Electric conductivity of  $\text{H}_3\text{PO}_4$  alone and when mixed with glucose in order to establish whether the additivity law is applicable or not.

Similar experiments have been performed with lactic, citric, nitric acids, so as to compare the results obtained with those of  $\text{H}_3\text{PO}_4$ .

TABLE No. 1

Temperature  $30^\circ$

Density of M/2 Glucose = 1.03126.

Molar volume of M/2 Glucose = 174.54.

M/2 Acid		Density		Molar Volume			Percentage Difference
		Acid	Acid + M/2 Glucose	Acid	Acid + M/2 Glucose		
					Calc.	Obs.	
Phosphoric	...	1.02632	1.05252	95.44	134.99	132.07	- 2.17
Lactic	...	1.01299	1.04281	88.84	131.69	129.46	- 1.70
Citric	...	1.03812	1.06511	202.19	188.36	183.17	- 2.75
Nitric	...	1.01445	1.04393	61.11	117.82	116.49	- 1.13

TABLE No. 2

Viscosity of M/2 Glucose = 1.2081

Temperature  $30^\circ$

M/2 Acid	Acid	Viscosity		Percentage Difference
		Acid + M/2 Glucose		
		Calc.	Obs.	
Phosphoric	... 1.1255	1.3336	1.3498	+ 1.21
Lactic	... 1.1213	1.3294	1.3542	+ 1.86
Citric	... 1.2243	1.4324	1.4802	+ 3.35
Nitric	... 1.0233	1.2314	1.2076	- 1.93

TABLE No. 3

Depression of the freezing point of M/2 Glucose =  $0.92^{\circ}$ 

M/2 Acid	Depression of freezing point			Percentage Difference	
	Acid	Acid + M/2 Glucose			
		Calc.	Obs.		
Phosphoric	...	1.14°	2.06°	2.20°	+ 6.79
Lactic	...	1.19°	2.11°	2.26°	+ 7.11
Citric	...	1.085°	2.005°	2.075°	+ 3.44
Nitric	...	1.85°	2.77°	2.90°	+ 4.51

TABLE No. 4

Substance	Conductivity	Conductivity × Viscosity	Percentage Difference
M/2 Phosphoric acid ...	0.029920	0.033670	—
„ + M/2 Glucose ...	0.025930	0.035000	+ 3.95
M/2 Lactic acid ...	0.004258	0.004774	—
„ + M/2 Glucose ...	0.003455	0.004648	- 2.63
M/2 Citric acid ...	0.007442	0.009111	—
„ + M/2 Glucose ...	0.005840	0.008645	- 5.11
M/2 Nitric acid ...	0.145400	0.148800	—
„ + M/2 Glucose ...	0.119400	0.144200	- 3.09

All these four physical properties studied lead to the conclusion that in cases of all the four acids when mixed with glucose, the additivity relationship is not maintained. Moreover it appears that a mixture of  $H_3PO_4$  and glucose produces an acid which is stronger than  $H_3PO_4$ . This is apparent from electric conductivity measurements after correction of viscosity increase. On the other hand all the other acids even after viscosity correction show a decrease in conductivity when mixed with glucose. This behaviour of phosphoric acid mixed with glucose is of the same type as that of boric acid when mixed with glycerol or carbohydrates.

# STUDIES IN HYDROUS ALUMINIUM OXIDE-PHOSPHORIC ACID AND HYDROUS FERRIC OXIDE-PHOSPHORIC ACID NEUTRALIZATIONS

By

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on 28th December 1955

Sesquioxides are formed in the process of weathering and are present in all soils either as separate particles or as coatings on other particles. These oxides exist in varying degrees of hydration. The fact that these oxides play an important role in the retention and fixation of added phosphates in soils has led to extensive studies on fixation of phosphates. Among the recent reviews on the fixation and retention of phosphate in soils were by Dean<sup>1</sup> and Wild<sup>2</sup>. The reaction of phosphate ions with the hydrous oxides of aluminium and iron was first believed to result in the precipitation of aluminium and iron phosphates. Some work in this direction was published by Gaarder<sup>3</sup>, Carter and Hartshorne,<sup>4</sup> and Ricca and Meduri<sup>5</sup> and phosphates possessing varying oxide :  $P_2O_5$  :  $H_2O$  ratio were identified. Another view has been put forward that the phosphate ions are merely attached to the surface of the hydrous oxide in an adsorption reaction. Reactions of phosphate ions with synthetic gel of alumina, ferric hydroxide and silica were studied by Gordon and Starkey.<sup>6</sup> Euler and Erikson<sup>7</sup> also investigated the adsorption of phosphoric acid on alumina gel. Kurtz, de Turk and Bray<sup>8</sup> regarded phosphate adsorption as a phenomenon of anion exchange. It has been suggested that the phosphate ions may be taken up by the hydrous aluminium and iron oxides with an equivalent release of the hydroxyl ions. Cole and Jackson<sup>9</sup> have identified compounds having the formulae  $Al(OH)_2 \cdot H_2PO_4$  and  $Fe(OH)_2 \cdot H_2PO_4$  by treating aluminium and iron salts with phosphates at pH 3.8 and 2.5 respectively. Most of the previous work on the hydrous oxides of aluminium and iron was carried on with the precipitates of aluminium and iron hydroxides suspended in water. The present work has been undertaken to find out the extent of reaction between hydrous oxides of aluminium and iron with phosphoric acid. In all these experiments air dried materials have been used.

## EXPERIMENTAL

Hydrous oxides of aluminium and iron were prepared by adding ammonium hydroxide to solutions of aluminium chloride and ferric chloride. The precipitates free from chloride ions were allowed to dry at room temperature. The solid thus obtained was pulverized in a pestle and mortar and sieved through 150 mesh sieve. The composition of the solids was  $Al_2O_3 = 66.00\%$  and  $Fe_2O_3 = 84.14\%$ . Equivalent amounts of the hydrous oxides were added to 25 ml of 0.1M, 0.2M, 0.5M and M acids in the oxide :  $P_2O_5$  ratio of 1:1, 2:1 and 3:1 in 250 ml Jena glass bottles. The mixture was shaken for one hour in a mechanical shaker and allowed to stand over for 24 hours at 30°. On the next day the solid was separated from the filtrate and analysed for acidic and basic constituents. Electrical conductivity and pH measurements were also carried on with the initial and final solutions.

*Electrical Conductivity measurements at 30°*

TABLE 1

Hydrous aluminium oxide-phosphoric acid system.

Initial specific conductivity $S \times 10^3$	Specific conductivity $\times 10^3$ after mixing in the ratio of		
	1:1	2:1	3:1
10.08	2.80	2.36	1.98
15.60	4.05	3.57	2.76
29.74	6.20	5.39	4.62
51.23	8.39	6.55	5.16

TABLE 2

Hydrous ferric oxide-phosphoric acid system

10.08	5.80	3.60	2.88
15.60	8.04	5.66	4.10
29.74	12.55	9.72	7.02
51.23	16.67	13.95	9.84

*pH measurements*

TABLE 3

Hydrous aluminium oxide-phosphoric acid system

Initial pH	pH after mixing in the ratio of		
	1:1	2:1	3:1
1.60	3.15	3.28	3.85
1.25	3.08	3.25	4.15
1.00	2.90	3.25	4.30
0.80	2.80	3.25	4.50

TABLE 4

Hydrous ferric oxide-phosphoric acid system

1.60	2.70	3.00	4.60
1.25	2.62	2.90	4.20
1.00	2.50	2.71	3.92
0.80	2.40	2.60	3.71

The analysis of the solid residues obtained after mixing hydrous aluminium and iron oxides with phosphoric acid is recorded below :

TABLE 5

Conc. of acid.	Molar ratio of oxide: $P_2O_5$	Nature of solid residue.	
		hydrous aluminium oxide, phosphoric acid system	hydrous ferric oxide, phosphoric acid system.
0.1M	1:1	2.8 $Al_2O_3$ : $P_2O_5$ : 5.3 $H_2O$	3 $Fe_2O_3$ : $P_2O_5$ : 7.2 $H_2O$
	2:1	4.0 $Al_2O_3$ : $P_2O_5$ : 5.5 $H_2O$	4.2 $Fe_2O_3$ : $P_2O_5$ : 12.6 $H_2O$
	3:1	4.8 $Al_2O_3$ : $P_2O_5$ : 7.2 $H_2O$	5.1 $Fe_2O_3$ : $P_2O_5$ : 16 $H_2O$
0.2M	1:1	2.5 $Al_2O_3$ : $P_2O_5$ : 5 $H_2O$	3 $Fe_2O_3$ : $P_2O_5$ : 7.7 $H_2O$
	2:1	3.7 $Al_2O_3$ : $P_2O_5$ : 4.2 $H_2O$	4 $Fe_2O_3$ : $P_2O_5$ : 12 $H_2O$
	3:1	4.8 $Al_2O_3$ : $P_2O_5$ : 7.1 $H_2O$	5 $Fe_2O_3$ : $P_2O_5$ : 17 $H_2O$
0.5M	1:1	2.5 $Al_2O_3$ : $P_2O_5$ : 5 $H_2O$	3 $Fe_2O_3$ : $P_2O_5$ : 7.7 $H_2O$
	2:1	3.6 $Al_2O_3$ : $P_2O_5$ : 4.2 $H_2O$	3.9 $Fe_2O_3$ : $P_2O_5$ : 13 $H_2O$
	3:1	3.7 $Al_2O_3$ : $P_2O_5$ : 4.2 $H_2O$	4.5 $Fe_2O_3$ : $P_2O_5$ : 16 $H_2O$
M	1:1	5 $Al_2O_3$ : 3 $P_2O_5$ : 10 $H_2O$	2.8 $Fe_2O_3$ : $P_2O_5$ : 7 $H_2O$
	2:1	2.5 $Al_2O_3$ : $P_2O_5$ : 2.5 $H_2O$	3.5 $Fe_2O_3$ : $P_2O_5$ : 11 $H_2O$
	3:1	3.3 $Al_2O_3$ : $P_2O_5$ : 4.3 $H_2O$	3.9 $Fe_2O_3$ : $P_2O_5$ : 13 $H_2O$

TABLE 6

Analysis of solutions after mixing is recorded below :

Conc. of acid.	Molar ratio of oxide to $P_2O_5$	Hydrous aluminium oxide phosphoric acid system	Hydrous ferric oxide phosphoric acid system.
		$Al_2O_3$ millimoles/litre	$Fe_2O_3$ millimoles/litre
0.1M	1 : 1	6.65	1.00
	2 : 1	2.32	0.25
	3 : 1	traces	traces
0.2M	1 : 1	18.37	3.50
	2 : 1	4.01	0.25
	3 : 1	traces	traces
0.5M	1 : 1	43.21	18.17
	2 : 1	12.32	0.50
	3 : 1	traces	traces
M	1 : 1	91.15	51.15
	2 : 1	34.03	6.12
	3 : 1	traces	traces

## DISCUSSION

The foregoing results clearly show that there is a marked difference between the behaviour of hydrous aluminium and ferric oxides with solutions of phosphoric acid. The freshly prepared hydrous oxide of aluminium appears to be more reactive and basic than the hydrous oxide of iron towards phosphoric acid. There has been a gradual fall in electrical conductivity in both the cases, when the hydrous oxides of aluminium and iron are added to phosphoric acid in the oxide :  $P_2O_5$  ratio of 1:1, 2:1 and 3:1. The conductivity changes are more marked in the case of hydrous aluminium oxide than hydrous iron oxide in all the phosphoric acid concentrations from 0.1M to M. From the conductivity data it is evident that more ions are disappearing from solutions of phosphoric acid in which hydrous aluminium oxide is added than in the case of hydrous ferric oxide.

The pH determinations indicate that the hydrogen ion concentration decreases with increasing amounts of the hydrous oxide added. It may be concluded from the pH measurements that, whatever the mechanism of removal of phosphate ions from solution be, it seems that hydrogen ions are being continuously adsorbed on the surface of the solid. The uptake of hydrogen ions being greater with greater additions of the hydrous oxides to phosphoric acid. The pH determinations further show that this adsorption is more pronounced with hydrous aluminium oxide than with hydrous ferric oxide.

The experimental results further show that appreciable amounts of hydrous oxides are dissolved in solutions of phosphoric acid. When freshly precipitated and air dried hydrous oxide of aluminium is added to equivalent amounts of phosphoric acid of different concentrations, apart from the adsorption of hydrogen and phosphate ions, the whole of the phosphate does not get precipitated as aluminium phosphate. In the resulting solution there is always some aluminium in the state of solution when the ratio of  $Al_2O_3 : P_2O_5$  is 1:1 and 2:1. On the other hand, when the molecular ratio is 3:1, there is no aluminium in solution. This can be explained from the following considerations.

The neutralization of hydrous aluminium oxide and phosphoric acid takes place according to the equation  $Al(OH)_3 + H_3PO_4 = AlPO_4 + 3H_2O$ . Due to hydrolysis, the neutralization is incomplete. As soon as some  $AlPO_4$  is formed, a part of it is hydrolysed into aluminium hydroxide and phosphoric acid and another part dissolves in free phosphoric acid with the formation of such complex compounds of phosphoric acid like  $H_3Al(PO_4)_2$ . The concentration of such a complex phosphoric acid will increase with the increase of free phosphoric acid in the system according to the law of mass action. In other words, in more concentrated solutions of phosphoric acid, the amount of complex formation of aluminium phosphate will be greater. This conclusion is supported by the experimental observations showing that the amount of aluminium remaining in solution increase with the increasing concentration of the acid. When the molecular ratio is 2:1, the complex formation also continues to take place, but the hydrolysis is more marked than in the previous case. On the other hand, when the ratio of  $Al_2O_3 : P_2O_5$  is 3:1, the amount of hydrous  $Al_2O_3$  being very large, the phosphoric acid is partially adsorbed by the unchanged hydrous oxide. This leads to a marked fall in the concentration of phosphoric acid in the system. Hence in this case the amount of phosphoric acid remaining in the solution being small the complex formation cannot be marked. This phenomenon is not only controlled by the amount of aluminium phosphate to form complexes with phosphoric acid but also depends upon the solubility product of  $AlPO_4$  and basicity of  $Al(OH)_3$ .

With hydrous ferric oxide, the neutralization takes place due to the formation of  $FePO_4$ . But this neutralization is less complete than in the case of hydrous

aluminium oxide, chiefly because ferric hydroxide is less basic in its action towards acids than aluminium hydroxide. The solubility product of  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  at  $18^\circ$  are  $1.1 \times 10^{-15}$  and  $1.1 \times 10^{-36}$  respectively. Also from the actual measurements it seems that the amount of iron existing in the state of solution in the neutralization of hydrous ferric oxide and phosphoric acid is less than in the case of hydrous aluminium oxide. This is perhaps due to smaller amounts of complex formation with iron than with aluminium phosphate. The conductivity measurements show that the electrical conductivity of the mixture of hydrous ferric oxide and phosphoric acid is always greater than the corresponding mixtures of hydrous aluminium oxide and phosphoric acid. This supports the view point that the neutralization is more complete with the comparatively stronger base  $\text{Al}(\text{OH})_3$  than with  $\text{Fe}(\text{OH})_3$ .

The analysis of the solid residues obtained after mixing the oxides with phosphoric acid also indicates that in the majority of cases the reaction is more pronounced and more complete in the case of hydrous aluminium oxide than with hydrous ferric oxide. The data shows that with hydrous ferric oxide, basic phosphates of varying composition are formed by reacting with phosphoric acid. The various products obtained have the  $\text{Fe}_2\text{O}_3 : \text{P}_2\text{O}_5$  ratio ranging from 2.8 to 5.1 and possessing varying degrees of hydration. On the other hand with hydrous aluminium oxide the products obtained have the  $\text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5$  ratio ranging from 1.6 to 4.8. In one case when the molecular ratio is 1:1 and the acid is molar, the solid obtained corresponds to  $5\text{Al}_2\text{O}_3 \cdot 3\text{P}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$  or  $3\text{AlPO}_4 \cdot 2\text{Al}(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ . In other cases the resulting product is more basic than the above one.

Aluminium existing in the soil solution has been found to be toxic to plants. Advocates of the superphosphate industry have pushed their view-point that on adding superphosphate (which contains water soluble monocalcium phosphate and which is highly acidic) or other soluble phosphates to soil, the toxic ions of aluminium are precipitated by the formation of aluminium phosphate. On the other hand, the results obtained by the interaction of hydrous aluminium and iron oxides with phosphoric acid, discussed in the foregoing lines, show that more aluminium passes into solution than iron oxide. In other words, by adding superphosphate which produces phosphoric acid in considerable quantities according to  $\text{Ca}(\text{H}_2\text{PO}_4)_2 = \text{H}_3\text{PO}_4 + \text{CaHPO}_4$ , there is some chance of the toxic aluminium ion passing into solution. However, the soil is such a complicated mixture that many other factors have also to be taken into account and the exact stage to which the above process may be applicable is difficult to predict.

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# STUDIES IN TITANIUM, IRON, CALCIUM, STRONTIUM, BARIUM, ZINC AND MANGANESE PHOSPHATES

By

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In these laboratories we are investigating the properties of various sparingly soluble phosphates and in this communication, some of our results and conclusions are recorded.

A study of the interaction of a solution of the titanium chloride ( $\text{TiCl}_4$ ) with phosphate solutions under different pH values has been made at the temperature of water bath ( $100^\circ$ ). It has been observed that the precipitate of titanium phosphate formed under this condition dried at room temperature is of the composition  $2\text{TiO}_2 \cdot \text{P}_2\text{O}_5 \cdot 10.6 \text{H}_2\text{O}$ .

The titanium phosphate precipitated in alkaline medium undergoes hydrolysis, becomes more basic and has the composition  $2.7 \text{TiO}_2 \cdot \text{P}_2\text{O}_5$ . It has been observed that the titanium phosphate undergoes hydrolysis in water and the addition of  $\text{CaCO}_3$  increases the hydrolysis and more phosphoric acid passes in the solution.

Neutral salts do not have any appreciable influence on increasing the solubility of titanium phosphate but they cause a feeble decrease in solubility.

Alkali solutions have a decomposing influence on the titanium phosphate liberating the corresponding amount of phosphoric acid in the solution.  $\text{NaOH}$  causes the maximum decomposition followed by  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$ . Carbonic acid has no marked influence on increasing the solubility of the titanium phosphate but a slight decrease in the solubility of the phosphate in water is observed. Hence titanium phosphate behaves like ferric phosphate. Acetic, tartaric and citric acids increase the solubility of the phosphate. Citric acid causes the maximum solubility of the phosphate followed by tartaric and acetic acids.

Barium, strontium, tricalcium, dicalcium, manganese, zinc, ferric and ferrous phosphates have been found to undergo hydrolysis in water. The hydrolysis of the phosphates increases with increase in temperature and with decrease in the ratio of the solid phosphate to water. With respect to the ability of the phosphates to hydrolyse, they can be placed in the following decreasing order :—  
 $\text{Sr}(\text{PO}_4)_2 > \text{Ca}_3(\text{PO}_4)_2 > \text{Zn}_3(\text{PO}_4)_2 > \text{FePO}_4 > \text{CaHPO}_4 > \text{Ba}_3(\text{PO}_4)_2 > \text{Mn}_3(\text{PO}_4)_2 > \text{Fe}_3(\text{PO}_4)_2$ .

Addition of  $\text{CaCO}_3$  checks the hydrolysis of the phosphates of barium, strontium, tricalcium, dicalcium, manganese and zinc, while ferric phosphate is more hydrolysed and more of the phosphoric acid is liberated in the solution. Ferrous phosphate is very slightly affected. Neutral salts increase the solubility of barium, strontium, tricalcium, dicalcium, manganese and zinc phosphates. The sulphates cause the maximum solubility followed by the chlorides and nitrates. While with basic radicals the decreasing order of solubility is  $\text{NH}_4 > \text{Na} > \text{K}$ .

On the other hand, ferric and ferrous phosphates do not show any marked influence. The solubility of ferric phosphate is slightly decreased in some cases.



Carbonic acid increases the solubility of the barium, strontium, tricalcium, dicalcium, manganese and zinc phosphates, while it has a feeble depressing effect on the solubility of ferric phosphate. Ferrous phosphate is not affected.

The organic acids viz. acetic, tartaric and citric increase the solubility of of the barium, strontium, tricalcium, manganese, and zinc phosphates to a such greater extent than ferric and ferrous phosphates. Ferrous phosphate is more soluble than the ferric phosphate. The maximum solubility of the phosphates is caused by citric acid followed by tartaric and acetic acids.

Alkali solutions,  $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  exert much greater decomposing influence on manganese, zinc, ferric and ferrous phosphates, than barium, strontium, tricalcium and dicalcium phosphates; stronger alkali decomposes more, liberating the corresponding amounts of phosphoric acid in the solution. Thus the maximum decomposition is observed with  $\text{NaOH}$  and the minimum with  $\text{NaHCO}_3$ .

$\text{TiO}_2$  and ilmenite adsorb phosphate ions from phosphate solutions in acidic as well as in alkaline media. The extent of adsorption depends on the concentration and the pH of the solution. With increase in concentration and decrease in pH the adsorption increases. Ilmenite adsorbs more phosphate than  $\text{TiO}_2$  and the adsorption follows the Freundlich adsorption isotherm.

When phosphoric acid of concentrations 4M to 0.04M is neutralized with  $\text{Ca(OH)}_2$ ,  $\text{Sr(OH)}_2$ ,  $\text{Ba(OH)}_2$ ,  $\text{ZnO}$  at  $30^\circ$ , in case of calcium when the molecular ratio of  $\text{CaO:P}_2\text{O}_5$  is 1:1 and 2:1 in most of the cases diphosphate of calcium is formed only in very dilute solutions. With concentrations 0.1M and 0.04M in the molar ratio 1:1 the monocalcium phosphate is formed. When the molecular ratio of  $\text{SrO}_3:\text{P}_2\text{O}_5$  is 1:1, at all concentrations only the monophosphate is formed, while in the ratio 2:1 the diphosphate is always generated. With barium, however at all the concentrations in the molecular ratio is 1:1 and 2:1 only the diphosphate is formed; when the molecular ratio of the metallic oxides to phosphorous pentoxide is 3:1 in all the three cases at all the concentrations a mixture of di and triphosphates are formed. In case of calcium, the amounts of di and triphosphates are nearly half and half, with strontium less of triphosphate and more of diphosphate are formed when the neutralization is carried in the 2:1 ratio.

The optimum concentrations of the phosphoric acid which give the maximum yield of the diphosphates are M and 0.51M in case of calcium and barium and 2M in case of strontium.

In case of zinc at all the concentrations of the phosphoric acid and in all the molar ratios only the triphosphate is formed and at no stage a di or monophosphate is formed,

# INFLUENCE OF CALCIUM CARBONATE AND SOME OXIDES ON THE SOLUBILITY OF SPARINGLY SOLUBLE PHOSPHATES

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As calcium carbonate is generally associated with calcium phosphates, the influence of  $\text{CaCO}_3$  on the solubility of calcium phosphate has been studied. Bassett<sup>1</sup> suggested that the depressing effect of  $\text{CaCO}_3$  on the phosphate solubility was due to formation of a stable hydroxy apatite mixed with various proportions of  $\text{CaCO}_3$ . McGeorge and Breazeale<sup>2</sup> pointed out that a chemical reaction between  $\text{CaCO}_3$  and calcium phosphate took place resulting in the formation of  $\text{Ca}_3(\text{PO}_4)_2$ .  $\text{CaCO}_3$ . But such a compound was not identified by them. Boischot<sup>3</sup> studied the action of soluble phosphates on  $\text{CaCO}_3$  and concluded that the initial reaction was the adsorption of phosphate on the surface of  $\text{CaCO}_3$ .

It seems that the liberation of  $\text{P}_2\text{O}_5$  from other sparingly soluble phosphates in presence of oxides such as  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  has not been investigated and hence this investigation has been taken up.

## EXPERIMENTAL

1 gm each of tricalcium phosphate, dicalcium phosphate (anhydrous), trimagnesium phosphate, dimagnesium phosphate (trihydrate), aluminium phosphate and ferric phosphate was taken in 250 ml. Jena glass bottles and 0.25 and 0.50 gm each of  $\text{CaCO}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  was added to the various bottles. The contents were shaken with 100 ml of double distilled water for one hour in a mechanical shaken and allowed to stand over for 24 hours at  $30^\circ$ . On the next day the clear supernatant liquid was filtered and the concentration of  $\text{P}_2\text{O}_5$  was determined volumetrically by using ammonium molybdate. We have observed that the phosphates of calcium, magnesium, aluminium and iron are copiously hydrolysed and the phenomenon of hydrolysis continues for a very long time, and their solubility is mainly caused by hydrolysis. Hence in these experiments the so called solubility of  $\text{P}_2\text{O}_5$  has been determined after a fixed interval of time in every case and a complete regularity is maintained so that the errors in solubility due to variation in time of contact of the phosphate and the solution may be minimised.

TABLE 1

Phosphate		$P_2O_5$ (gms/litre) with water alone	$P_2O_5$ gms/litre after adding	
			0.25 gms of $TiO_2$	0.50 gms of $TiO_2$
Aluminium phosphate	...	0.0974	0.0970	0.0952
Ferric	„	0.0449	0.0449	0.0445
Tricalcium	„	0.1293	0.1293	0.1260
Dicalcium	„	0.0509	0.0500	0.0495
Trimagnesium	„	0.2800	0.2800	0.2800
Dimagnesium	„	0.4250	0.4250	0.4180

TABLE 2

Phosphate		$P_2O_5$ gms/litre after adding			
		0.25 $CaCO_3$	0.50 $CaCO_3$	0.25 $CaO$	0.50 $CaO$
Aluminium phosphate	...	0.0990	0.1065	0.0986	0.1095
Ferric	„	0.0500	0.0575	0.0556	0.0637
Tricalcium	„	0.0320	0.0285	0.0330	0.0230
Dicalcium	„	0.0375	0.0290	0.0301	0.0250
Trimagnesium	„	0.1630	0.1325	0.0975	0.0905
Dimagnesium	„	0.0612	0.0485	0.0373	0.0245

TABLE 3

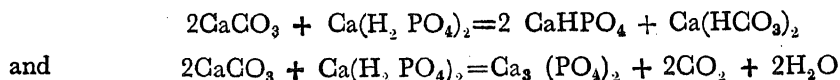
		0.25 $Al_2O_3$	0.50 $Al_2O_3$	0.25 $Fe_2O_3$	0.50 $Fe_2O_3$
Aluminium phosphate	...	0.0550	0.0405	0.0750	0.0701
Ferric	„	0.0440	0.0415	0.0230	0.0152
Tricalcium	„	0.1293	0.1293	0.0640	0.0605
Dicalcium	„	0.0500	0.0480	0.0500	0.0485
Trimagnesium	„	0.2800	0.2800	0.2800	0.2800
Dimagnesium	„	0.4200	0.3955	0.3585	0.3372

TABLE 4

Phosphate		0.25 $ZnO$	0.50 $ZnO$	0.25 $MgO$	0.50 $MgO$
Aluminium phosphate	...	0.0364	0.0295	0.0790	0.0705
Ferric	„	traces	traces	traces	traces
Tricalcium	„	traces	traces	traces	traces
Dicalcium	„	0.0190	0.0152	„	„
Trimagnesium	„	0.1115	0.1035	„	„
Dimagnesium	„	0.0992	0.0975	„	„

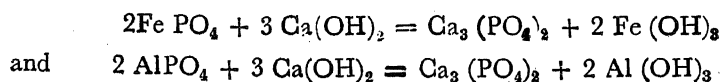
## DISCUSSION

From table 2 it is evident that both CaO and CaCO<sub>3</sub> depress the solubility of the phosphates, except for ferric and aluminium phosphates. With increasing amounts of CaO and CaCO<sub>3</sub> added, there is a gradual decrease in P<sub>2</sub>O<sub>5</sub> concentration in the solution. The depressing effect in the case of calcium phosphates is due to the fact that hydrolysis of the calcium phosphates is checked by the presence of CaO and CaCO<sub>3</sub> which are alkaline. For example tricalcium phosphate can hydrolyse as  $4 \text{Ca}_3(\text{PO}_4)_2 + 3 \text{H}_2\text{O} \rightleftharpoons 3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2 \cdot 3\text{H}_2\text{O} + 3\text{H}_3\text{PO}_4$ . When an excess of CaO or CaCO<sub>3</sub> is added to the above system, back reaction takes place according to the law of mass action, resulting in the formation of unhydrolysed calcium phosphate. This is why more soluble phosphate or free phosphoric acid is not allowed to remain in the solution. Moreover, the reaction of CaCO<sub>3</sub> with the monocalcium phosphate in solution produced by the hydrolysis of tricalcium phosphate may result again in the formation of di and tri phosphates according to:—



The formation of less soluble di and tri phosphates in neutral soils containing CaCO<sub>3</sub>, when superphosphate is added to it, is also due to the above mechanism.

The reaction of CaO and CaCO<sub>3</sub> with magnesium phosphates has been observed to be similar to calcium phosphates, but with aluminium and iron phosphates the concentration of P<sub>2</sub>O<sub>5</sub> in solution has been observed to increase, with increasing concentration of CaO and CaCO<sub>3</sub>. This is due to the fact that CaO and CaCO<sub>3</sub> partially decompose the phosphate of iron and aluminium. Lime dissolves appreciably in water and reacts with iron and aluminium phosphates resulting in the formation of more soluble calcium phosphates according to:—



Moreover, as the solubility products of ferric and aluminium hydroxides are much smaller than those of calcium and magnesium hydroxides, the OH<sup>-</sup> ions available in the system readily react to form insoluble ferric and aluminium hydroxides. Similarly, CaCO<sub>3</sub> decomposes the phosphates of aluminium and iron forming the hydroxide of the metal, carbonic acid and calcium phosphate. Because the amount of OH<sup>-</sup> ions is much greater in presence of lime than CaCO<sub>3</sub>, the possibility of the decomposition of iron and aluminium phosphate forming the respective hydroxides is greater with lime than with CaCO<sub>3</sub>. The results also show that more P<sub>2</sub>O<sub>5</sub> has passed into solution with CaO than with CaCO<sub>3</sub>. Moreover, the hydrolysis of the phosphates of the alkaline earth metals is checked to a greater extent by CaO than by CaCO<sub>3</sub>.

The beneficial effects of basic slag on acidic soils can also be explained from these considerations. Acidic soils contain iron, aluminium and titanium phosphates in varying proportions. When basic slag is added to such a soil the lime present in the basic slag can readily decompose the phosphates of iron, aluminium and titanium and convert them into calcium phosphates which is much more soluble than the phosphates of iron, aluminium and titanium. In other words, basic slag can not only supply small amounts of P<sub>2</sub>O<sub>5</sub> when added to soil, but it also becomes a producer of tricalcium and magnesium phosphates in acidic soils.

It is also obvious from the data that  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  exert smaller influence upon the solubility of phosphates than  $\text{CaO}$  and  $\text{CaCO}_3$ . Table 1 indicates that  $\text{TiO}_2$  has very little influence on the solubility of phosphates, and for all practical purposes the amount of  $\text{P}_2\text{O}_5$  in solution is nearly the same as with water alone.  $\text{ZnO}$  and  $\text{MgO}$  have been observed to influence the solubility of these phosphates considerably because zinc hydroxide and magnesium hydroxide are appreciably alkaline in solution and therefore can check the hydrolysis of phosphates of alkaline earths. It is also apparent from the data that the depressing effect is greater with  $\text{MgO}$  than with  $\text{ZnO}$ . This is due to the fact that  $\text{Mg}(\text{OH})_2$  being more alkaline oxide than with zinc oxide.

It is interesting to state here that whereas  $\text{CaO}$  and  $\text{CaCO}_3$  are able to decompose the phosphates of aluminium and iron and increase the  $\text{P}_2\text{O}_5$  solubility, the oxides of zinc and magnesium are not able to decompose these phosphates. It seems that the behaviour of  $\text{CaO}$  is due to greater solubility of lime in water than magnesia or zinc hydroxide. The solubility products of  $\text{Ca}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$  and  $\text{Zn}(\text{OH})_2$  are respectively  $4.8 \times 10^{-5}$ ,  $1.2 \times 10^{-11}$  and  $1.8 \times 10^{-14}$ . As has already been pointed out, the  $\text{OH}^-$  ions liberated by lime in water react with ferric phosphate to produce ferric hydroxide and calcium phosphate. On the other hand, the  $\text{OH}^-$  ions liberated by magnesia in water being small are not adequate enough to decompose the ferric and aluminium phosphates as in the case of lime. Consequently, on adding lime to ferric phosphate suspended in water, there is an appreciable increase in the phosphate content in the state of solution, but with  $\text{MgO}$  the position is different.  $\text{MgO}$  and  $\text{ZnO}$  markedly decrease the phosphate content of iron and aluminium phosphates in contact with water because the  $\text{OH}^-$  ions set free from  $\text{Mg}(\text{OH})_2$  and  $\text{Zn}(\text{OH})_2$  are small and inadequate to set up a double decomposition between the  $\text{OH}^-$  ions and the sparingly soluble phosphate. Moreover, the free phosphoric acid existing in the suspensions of aluminium and iron phosphates is absorbed and partially neutralized by the hydroxides of zinc and magnesium forming the sparingly soluble phosphates of zinc and magnesium. Zharovskii<sup>5</sup> has recorded the solubility product of zinc phosphate to be  $9.1 \times 10^{-33}$ . It appears that the addition of  $\text{ZnO}$  to aqueous suspensions of other sparingly soluble phosphates also results in the formation of  $\text{Zn}_3(\text{PO}_4)_2$  by the combination of  $\text{Zn}^{++}$  and  $\text{PO}_4^{--}$  ions in solution because its solubility product is very low.

In soils along with  $\text{CaCO}_3$ ,  $\text{MgCO}_3$  is frequently present. Moreover, phosphatic fertilizers are frequently being manufactured from materials containing dolomite. In many parts of the world, there are soils containing more  $\text{MgO}$  than  $\text{CaO}$ . From our investigations it is evident that  $\text{MgO}$  unlike  $\text{CaO}$  is unable to decompose the almost unavailable phosphates of iron and aluminium into more readily available phosphates of magnesium. On the other hand,  $\text{MgO}$  and  $\text{ZnO}$  are observed to depress their solubility. In this respect lime is certainly more useful than  $\text{MgO}$  or  $\text{ZnO}$  in helping phosphate nutrition in plants growing in soils containing aluminium and iron phosphates.

The effect of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  upon the solubility of different phosphates is very small and is nearly of the same order. It is probable that the slight depressing effect of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  is due to adsorption of phosphoric acid on their surfaces.

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# INFLUENCE OF DIFFERENT PHOSPHATES IN COMPOSTING OF WHEATSTRAW, SAWDUST AND MIXTURES OF SAWDUST WITH STRAW AND DUNG

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In a previous publication we<sup>1</sup> have shown that on the addition of finely divided phosphate rock or basic slag or superphosphate to plant materials to be composted, there is a greater increase in the fixation of atmospheric nitrogen in the process of composting than in the absence of phosphates. Also, the availability of the phosphate rock or basic slag is increased. In other words, the compost obtained by a mixture of organic matter and calcium phosphate is richer in total nitrogen, available nitrogen and available phosphate than that obtained in the absence of calcium phosphate. The composts obtained with phosphates may contain 1.8 to 2% total nitrogen, whilst the Howard composts usually contain 0.8 to 1% total nitrogen.

Moreover, we have observed that the compost obtained from straw along with phosphates does not lose nitrogen as readily as those obtained from weeds and calcium phosphate. It seems that organic substances rich in lignin, when mixed with calcium phosphates, form more stable composts than those obtained from soluble carbohydrates and celluloses mixed with finely divided rock phosphate or basic slag.

We have continued further work on this subject and have studied the composting of straw and sawdust, rich in lignin, under different conditions. Also, we have studied the carbon-nitrogen transformations of straw mixed with water in presence or absence of small doses of urea kept at a temperature of 35°.

## EXPERIMENTAL PROCEDURE

The composting was carried on in wooden boxes. The joints and openings were closed with a paste to stop any leakage from sides and the bottom. The material to be composted was weighed and then put into the boxes. Samples of materials were previously taken and the dry matter estimated. The requisite amount of soil, i. e. 1/8th soil of the total weight of the material was added mixed well with or without phosphates. The moisture was kept at 60% level. The compost was kept moist throughout the composting period. The temperature was recorded daily and the moisture made up. After composting was continued for a definite period, the whole material was weighed and then a known weight of the samples was taken out for analysis.

The total carbon was estimated by the method of Robinson, McLean and Williams<sup>4</sup> and the total nitrogen was estimated by the Kjeldahl method modified by Treadwell and Hall<sup>5</sup> using salicylic acid for reduction of nitrites and nitrates.

PERCENTAGE ANALYSIS ON DRY BASIS

		Sawdust	Soil	Wheat straw
Total carbon	...	44.90	0.435	30.5
Total nitrogen	...	0.69	0.040	0.618
C/N ratio	...	65	10.8	49.4

The experimental temperatures varied from 20° to 30°. The experimental results are recorded below:—

*Composting of Sawdust*

6 Kilograms sawdust + 750 grams soil

Period of incubation in days	Total carbon (%)	Total nitrogen (%)	Total carbon (gms.)	Total nitrogen (gms.)	Total carbon oxidised (gms.)	Increase of total nitrogen (gms.)	Total carbon oxidised (%)	Increase of total nitrogen (%)	C/N ratio
0	39.9	0.617	2697.6	41.70	...	...	...	...	64
225	35.3	0.699	2153.3	42.63	544.3	0.93	20.1	2.2	50
400	31.8	0.851	1599.3	42.68	1098.3	0.98	40.7	2.3	37
600	29.2	0.941	1314.6	42.43	1383.0	0.73	51.2	1.7	32

2.5 Kilograms Wheat straw + 312.5 grams. soil

0	33.51	0.592	952.5	16.82	...	...	...	...	56.6
190	26.20	0.980	482.0	18.03	470.5	+1.11	49.3	+6.5	26.6
290	20.10	1.240	270.0	16.80	655.5	-0.02	68.8	-0.11	16.0

2.5 Kilograms Wheat straw + 312.5 grams soil + 14.64 Kilograms  $P_2O_5$  as Trichinopoly rock phosphate per ton of organic matter

0	32.3	0.567	952.5	16.82	...	...	...	...	56.9
190	26.4	1.400	377.5	20.02	506.1	+3.20	60.3	+19.0	18.8
290	18.6	1.480	239.2	19.15	712.3	+2.33	74.4	+13.8	12.0

2.5 Kilograms Wheat straw + 312.5 soil + 14.64 Kilograms  $P_2O_5$  as Tata basic slag per ton of organic matter

0	29.81	0.526	952.5	16.82	...	...	...	...	56.6
190	24.80	1.140	446.4	20.52	506.1	+3.70	53.1	+21.9	21.2
290	17.07	1.440	227.0	19.20	725.5	+2.38	76.1	+14.1	11.7

6 Kilograms Sawdust + 750 grams soil + 14.64 Kilograms  $P_2O_5$  as  
Trichinopoly rock phosphate per ton of organic matter

Period of incubation in days	Total carbon (%)	Total nitrogen (%)	Total carbon (gms)	Total nitrogen (gms.)	Total carbon oxidised (gms.)	Increase of total nitrogen (gms.)	Total carbon oxidised (%)	Increase of total nitrogen (%)	C/N ratio
0	38.5	0.589	2697.6	41.70	...	...	...	...	65.3
225	33.5	0.730	2137.9	46.58	599.7	4.88	20.7	11.7	45.8
400	30.0	0.910	1542.3	46.63	1155.3	4.93	42.8	11.8	33.0
600	28.2	1.000	1311.8	46.52	1385.8	4.82	51.2	11.5	28.2

6 Kilograms Sawdust + 750 grams soil + 14.64 Kilograms  $P_2O_5$  as  
Tata basic slag per ton of organic matter

0	35.3	0.545	2697.6	41.70	...	...	...	...	4.7
225	31.2	0.721	2058.4	47.54	639.2	5.84	23.7	14.0	43.2
400	28.8	0.890	1542.2	47.66	1155.4	5.96	42.8	14.3	32.4
600	26.9	1.008	1263.7	47.35	1433.9	5.65	53.1	13.5	26.6

3 Kilograms Wheat straw + 3 Kilograms sawdust + 750 grams soil

0	36.20	0.58	2448.6	39.48	...	...	...	...	61.9
225	31.20	0.80	1759.6	45.68	689.0	6.20	28.1	15.7	38.5
400	28.84	0.95	1378.5	45.69	1070.1	6.21	44.0	15.7	30.2
600	24.76	0.96	1151.5	44.60	1297.1	5.12	52.9	12.9	25.8

3 Kilograms Sawdust + 12 Kilograms Dung + 1875 grams soil

0	28.50	0.895	2198.0	69.31	...	...	...	...	31.7
225	22.41	1.380	1376.8	84.78	821.2	15.47	37.7	22.3	15.0
400	18.40	1.510	990.4	81.22	1207.6	11.91	54.9	17.1	12.1
600	17.21	1.510	863.0	77.08	1335.0	7.71	60.7	11.2	11.3

A very remarkable fact has been observed by us in these composting experiments. The amount of nitrogen increased by fixation in these composts is always greater when the added soil is low in nitrogen status. Soils rich in nitrogen, when added to the compost, produce small fixation of atmospheric nitrogen.



The foregoing experimental results clearly show that in the composting of sawdust rich in lignin mixed with small amounts of soil, there is appreciable fixation of nitrogen in this process. In presence of finely divided rock phosphate or basic slag, the fixation of atmospheric nitrogen is greater than in the absence of phosphates. Moreover, there is fixation of atmospheric nitrogen in the composting of mixture of dung and sawdust or straw and sawdust. In this case also, the nitrogen fixation is accentuated by adding calcium phosphates. But, in presence of large amounts of phosphates in the system, more or less stable phospho-proteins are formed by the combination of proteins and phosphorus compounds. These compounds seem to resist ammonification, nitrification and loss of nitrogen better than proteins alone. This appears to be an important reason why the efficiency of nitrogen fixation in soils or in compost heaps appears to be larger in presence of increasing quantities of phosphates.

In the following tables some of our results on nitrogen fixation and nitrogen conservation have been summarised. The results show that nitrogen conservation in the composting of quickly decomposing fresh green materials like weeds and water hyacinth is appreciably greater in presence of phosphates than in their absence. Similarly, in composting dung, straw, sawdust containing lignin, the nitrogen fixation in presence of phosphates is appreciably greater than in their absence.

Composting experiments			Initial C/N ratio.	Final nitrogen % (Dry basis).	Nitrogen conservation %
1.	Weeds + Soil	...	12.7	0.700	43.2
2.	Water hyacinth alone	...	17.6	2.500	54.5
3.	Cowdung + Soil	...	27.9	1.110	102.5
4.	Wheat straw + Soil	...	49.6	1.070	110.5
5.	Wheat straw + Soil	...	56.6	0.950	106.5
6.	Sawdust + Straw + Soil	...	61.9	1.120	115.7
7.	Sawdust + Straw + Soil	...	114.7	0.590	117.8

The materials used in the above Table when mixed with Phosphates

1.	Weeds + Rock phosphate (Trichinopoly).	12.7	0.800	44.8
2.	Water hyacinth + Rock phosphate (Trichinopoly).	17.6	2.850	64.9
3.	Cowdung + Rock phosphate (Trichinopoly).	17.9	1.180	105.7
4.	Wheat straw + Rock phosphate (Trichinopoly).	49.4	1.183	129.2
5.	Wheat Straw + Rock phosphate (Trichinopoly).	56.3	1.400	119.0
6.	Sawdust + Straw + Rock phosphate (Trichinopoly).	61.9	1.120	129.9
7.	Sawdust + Straw + Algerian rock phosphate.	114.7	0.835	130.9

Composting experiments	Initial C/N ratio	Final nitrogen % (Dry basis	Nitrogen conservation %
1. Weeds + Superphosphate ...	12.7	1.050	45.3
2. Water hyacinth + Tata basic slag.	17.6	2.550	66.4
3. Cowdung + Tata basic slag.	17.9	1.200	106.8
4. Wheat straw + Superphosphate + Rock phosphate.	49.4	1.200	138.2
5. Wheat straw + Tata basic slag.	56.6	1.140	121.9
6. Straw + Sawdust + Tata basic slag.	61.9	0.880	136.7
7. Straw + Sawdust + Tata basic slag.	114.7	0.875	130.5

#### *Nitrogen fixation in the incubation of straw*

In some interesting experiments in the incubation of straw at 36° or 26°, Hutchinson and Richards<sup>2</sup>, in their researches on the preparation of artificial farm-yard manure, recorded the following observations :—

	Temperature.	Loss of dry matter. %	Nitrogen		Efficiency.	Loss (-) or gain ( ).
			Initial (mgms.)	Final (mgms.)		
Straw with water ...	36°	40.1	71	97	16	26
(I) Straw with urine ...	26°	49.1	507	178	...	- 329
Straw with urine ...	36°	59.8	507	176	...	- 331

*Number of experiments*

		1	2	3	4	5				
		nitrogen (mgms.)	nitrogen (mgms.)	nitrogen (mgms.)	nitrogen (mgms.)	nitrogen (mgms.)				
At beginning	...	77.5	157.0	237.6	317.6	397.6				
(II) Straw and urine nitro- gen after 86 days.		77.3	153.1	226.8	262.1	308.0				
(III) The decomposition of straw in presence of varying quantities of nitrogen as urea.										
Treatments at beginning.	1	2	3	4	5	6	7	8	9	10
Straw nitrogen (mgms).	71	71	71	71	71	71	71	71	71	71
Urea nitrogen...	0	5	10	24	48	97	243	486	729	973
Total nitrogen	71	76	81	95	119	168	314	557	800	1044
After 3 months organic nitro- gen (mgms)..	180	177	174	190	192	171	245	269	181	134
Ammonia ...	0	5	2	4	4	29	74	68	71	76
Total ...	180	182	176	194	196	200	319	337	252	210
Gain or loss ...	109	106	95	99	77	32	5	-220	-558	-834
Dry matter loss%	49	46	45	49	47	53	51	48	19	14
Efficiency calcu- lated by us,(i.e., nitrogen fixed in milligrams per gram of carbon oxidized)	57	58	67	52	42	15	2.5	...	...	...

The efficiency recorded above is very high and is much higher than that observed in series (I), i.e. 16. We have not so far obtained such high fixation in our experiments in composting or incubation of straw, but higher fixations have been obtained by us<sup>6</sup> in our nitrogen fixation experiments, specially in presence of sunlight and calcium phosphates by ploughing in organic matter in soil or incorporating organic matter in soil or sand in dishes.

In discussing the observations recorded in series no. (I), the authors stated as follows:—

“The three equal portions of straw were saturated either with water or urine and allowed to ferment for 3 months in the laboratory, the two portions with urine being subjected to different temperatures. As will be seen

from the foregoing table, these two portions fermented to different degrees—the dry matter losses being 49 and 60% respectively but the final nitrogen content was almost identical and practically 3/4th. of the nitrogen supplied as urine was lost”.

Regarding the results recorded in series no. (II), Hutchinson and Richards have stated as follows :—

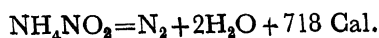
“The above results show that losses of nitrogen occurring after satisfactory rotting do not exceed 4% in the lower concentrations of nitrogen. The ordinary losses of the manure heaps are frequently more than tenfold this amount”.

Discussing the results recorded in series no. (III), the authors reported as follows :—

“Ten portions of straw were moistened to the same extent and while one received water only, the others received additions of soluble nitrogen in the form of urea in varying quantities until the last portion was saturated with a solution similar in concentration of nitrogen to that of horse urine (1% nitrogen). The different portions were kept in an incubator for 3 months, at the end of which time it was evident that contrary to expectation, the straw without or merely with low doses of nitrogen, had passed through a marked rotting process. On analysis it was found that there had been a definite accumulation of nitrogen in the lower members of the series, while the higher members had lost in some cases the greater portion of their original nitrogen. In seven out of the ten cases the final nitrogen of the fermented straw varied only between 180 to 210 mgms. irrespective of the nitrogen content of the original mixture. It should also be noted that the extent of the rotting, *i.e.*, loss of dry matter, in experiments 1—8 was very much greater than in 9 and 10 in which the straw was subjected to the action of solutions closely approaching the concentration of ordinary urine, the high alkalinity of the latter exercising a check on decomposition. In the main, the nitrogen retained by super-saturated straw or such as is accumulated by undersaturated straw, as in nos. 1—6 in the above table, appears to be stored up in organic or non-ammoniacal form. The maximum retention has been found to occur within the first 4 weeks, after which time breakdown of this organic nitrogen to ammonia and consequent loss by volatilisation seems to keep pace with loss of dry matter. Finally, the material assumes a “stabilised” condition—the loss of nitrogen becomes greatly diminished or may be absent altogether for long periods. It may be stated that when straw has worked from an unsaturated to a stable phase little or no free ammonia is to be found, but straw which commences with a super-abundance of nitrogen appears to hold when in a fermented state, upwards of 14% of its nitrogen in the form of ammonia so long as the material is in a moist condition. Desiccation leads almost to complete loss of ammonia and in this respect as well as in the proportion of ammonia in the moist material, the artificial resembles the natural manure. From the study of the inter-relations between nitrogen and straw, we have come to the conclusion that the amount of nitrogen necessary for pronounced rotting, the amount which straw is capable of fixing in the form of ammonia are identical and that in general the figure varies only between 0.70 and 0.75 parts of nitrogen per 100 parts of dry straw”.

From the foregoing quotations it is quite clear that Hutchinson and Richards have not been able to explain at all the increase in the nitrogen content of straw moistened with water alone or containing small amount of urea. The most interesting point is that the carbonaceous matter present in the straw has undergone marked loss to the extent of 40% in the series no. (I) and 49% in the series no. (III) even in the complete absence of urine or urea. There is no doubt that this loss of organic matter has been caused by the oxidation of the cellulose and other carbonaceous compounds. Dhai<sup>3</sup> was the first to explain this increase of nitrogen with straw alone from the viewpoint of atmospheric nitrogen fixation caused by the liberation of energy evolved in the slow oxidation of cellulose and lignin of straw. This oxidation process has liberated energy which has been actually utilised in fixing nitrogen by straw to the extent of 26 mgms in series no. (I) and 109 mgms. in series no. (III) in the complete absence of the additional nitrogenous substances. Increase of nitrogen varying from 106 mgms. upto 5 mgms. have taken place in presence of amounts of urea containing 5 to 243 mgms. nitrogen. These results are also due to the fixation of atmospheric nitrogen in the process of the loss of dry matter varying from 46 to 51%.

On the other hand, when the added urine or urea is in large concentrations, marked nitrification of the urea takes place and in this process the unstable substance, ammonium nitrite, is formed and decomposes according to the equations :—



This is certainly the most important cause of the losses of nitrogen recorded in the experiments of Hutchinson and Richards. There may be a small loss of nitrogen as ammonia gas.

We have repeated some of the experiments in the incubation of straw and our results are recorded below :—

*Analysis of wheat straw.*

Total carbon ..... 36.60%  
 Total nitrogen..... 0.616 % C/N ratio : 59.4  
 Total dry matter... 11.4 gms.

Incubated at 35°C for 3 months.

	Initial total nitrogen (mgms.)	Total nitro- gen after 3 months (%)	Total nitro- gen after 3 months (mgms.)	Increase in nitrogen (mgms.)	Loss of dry matter (%)
1. Straw + water	66.53	1.93	91.55	25.02	41.6
2. Straw + 5 mgms. urea nitrogen.	71.53	2.10	93.76	22.23	39.1
3. Straw + 10 mgms. urea nitrogen.	76.53	1.80	92.98	16.45	45.0
4. Straw + 24 mgms. urea nitrogen.	90.53	2.30	97.92	6.39	36.1

These experiments show that in every case marked fixation of nitrogen takes place at 35° after incubation for 3 months. The efficiency of nitrogen fixation in no. 1 is 14 whilst Hutchinson and Richards' value as calculated by us is 16.

From our experiments recorded in the foregoing pages and the above discussion, it is clear that from the preparation of stable composts both calcium phosphate and lignin are useful, and, such composts can be prepared from straw, dung and sawdust and calcium phosphates with fixation of atmospheric nitrogen. Green materials when incorporated in the soil mixed with calcium phosphates can readily fix atmospheric nitrogen but cannot build up humus permanently.

#### SUMMARY

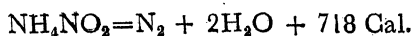
A rapid rise in the temperature of the mixture was observed in the beginning of composting with a slow downward gradient afterwards. In composting of wheat straw, sawdust rich in lignin or mixtures of sawdust and straw or sawdust and dung, when mixed with small amounts of soil, there is an appreciable fixation of nitrogen from air.

In presence of finely divided rock phosphate or basic slag (32.4 lbs.  $P_2O_5$  per ton of organic matter), the fixation of nitrogen is greater than in absence of phosphates.

It will be observed that the efficiency of the process of nitrogen fixation, i.e. the amount of nitrogen fixed in milligrams per gram of carbon oxidised, of straw or sawdust, singly or in mixtures, is always greater in presence of phosphates. Under ordinary conditions the proteins present or formed in nitrogen fixation undergo ammonification and nitrification which oppose the increase of proteins in compost heaps and, thus, the amount of proteins remaining in compost heaps, tend to decrease. Consequently, the apparent efficiency falls.

It is interesting to note that the C/N ratio of the compost obtained in presence of phosphates is lower than of the compost prepared without phosphates.

The loss of nitrogen is due to the high temperature prevailing in the compost heaps and acidity produced during the decomposition of organic matter in heaps. These lead to the rapid decomposition of the unstable substance, ammonium nitrite, formed in the nitrification of nitrogenous compounds according to the following equation:—



The loss of nitrogen can be minimised if the temperature of the system and its acidity are not allowed to rise much. This can be achieved by turning the mass thrice a week. The temperature in these experiments did not exceed 37°, whilst, in the majority of methods of composting, the temperature rises beyond 70° leading to marked loss of nitrogen.

Experimental results show that incubation of straw mixed with 50% of its weight of water in glass beakers for 3 months leads to a fixation of atmospheric nitrogen of 37.7% of the total nitrogen present in the straw.

Even in presence of a small amount of urea, there is also appreciable fixation of atmospheric nitrogen in these incubation experiments of straw. The amount of fixation decreases as the concentration of urea increases. Similar increase in nitrogen is recorded in the experiments of Hutchinson and Richards in Rothamsted.

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# CONTRIBUTION A L'ETUDE DE LA STRUCTURE PHYSIQUE FINE DES PHOSPHATES NATURELS DE CHAUX

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La littérature scientifique concernant l'emploi direct des phosphates naturels comme engrais a apporté, dans les cinquante premières années du siècle, de nombreuses informations sur les facteurs liés au sol, à la plante et à l'environnement général, qui conditionnent l'assimilabilité de l'ion  $\text{PO}_4$  apporté par cette forme d'engrais.

Par contre, ce n'est que récemment que des travaux substantiels provenant notamment de l'école russe et de l'école française ont souligné le rôle essentiel que jouent dans ce système de définition les facteurs liés au phosphate lui-même.

Bien qu'en effet des travaux déjà anciens (Lebediantzew et autres) aient à très juste titre attiré l'attention sur les facteurs de dimensions tels que finesse de pulvérisation, il n'existe encore que peu de recherches concernant les définitions intrinsèques des minerais phosphatifiés et notamment des phosphates de chaux présentés à l'emploi direct comme engrais.

Cette dernière position du problème revêt cependant à l'examen une importance primordiale. En effet, des expériences d'assimilabilité sur cultures en pots, conduites avec toute la rigueur expérimentale nécessaire, tous facteurs liés au sol, à la plante et à l'environnement étant maintenus constants, ont démontré que, à quantité égale de  $\text{P}_2\text{O}_5$  présente dans l'engrais, l'assimilabilité de l'acide phosphorique pouvait varier en proportion considérable, et en pratique de 1 à 10, en fonction de la nature du gisement dont provenait l'échantillon utilisé comme engrais. Les échantillons de phosphates naturels qui ont servi à ces séries de comparaisons ont été choisis de façon à constituer une gamme aussi étendue que possible, allant des structures micro ou crypto-cristallines des gisements dits "tendres" de l'Afrique du Nord (Gafsa) aux formes eu-cristallines compactes des apatites de Kola.

Il est intéressant de noter que toutes les mesures d'ordre chimique (mesures de solubilité différentielle dans les réactifs chimiques ou conventionnels—acide formique, lactique, citrique), ou physique (densité apparente), ainsi que des mesures de capacité de mobilisation des ions  $\text{PO}_4$ —par mesure isotopique indirecte en présence de résines fixatrices d'ions  $\text{PO}_4$ ... ont confirmé la signification primordiale du facteur "origine" du point de vue de l'assimilabilité des phosphates naturels. (Comptes-rendus de la II. Assemblée Générale de l'Association Internationale d'Etudes Phosphatières, Blois 1955 sous presse).



Ces constatations expérimentales, quelle que soit leur importance, n'ont cependant pas encore de valeur réellement explicative. Il serait nécessaire de rendre compte des différences observées dans l'assimilabilité des variations concomitantes assignées, à l'intérieur du cadre général du concept phosphates naturels, compte tenu de la composition chimique totale, soit à la structure minéralogique et pétrographique, soit enfin à la structure géométrique ou au mode d'aggrégation microscopique ou infra-microscopique des échantillons proposés.

Les recherches dont les résultats bruts sont consignés cidessous ont eu pour objet d'élucider quelques problèmes de texture physique, posés en particulier à propos des phosphates nord-africains, indépendamment des recherches purement pétrographiques qui visent à rapporter les différences d'assimilabilité observées à la structure même des minéraux phosphatifères caractéristiques de chaque gisement.

#### PARTIE EXPERIMENTALE

Les échantillons de phosphate-soumis aux essais ont été les suivants :

Désignation	Spécification
A	Phosphate de Gafsa 30% $P_2O_5$ —tamis 100
B	„ „ „ — „ 300
C	„ Maroc 32% $P_2O_5$ — „ 100
D	„ „ „ — „ 300
E	„ „ 34% $P_2O_5$ — „ 100
F	„ „ „ — „ 300
G	„ Constantine (Agrophos)
H	„ Floride — tamis 300
I	„ Kôla „ 300
J	„ Gafsa 30% $P_2O_5$ — brut
K	„ Maroc 32% — „
L	„ „ 34% — „

Notons que les échantillons de phosphate de Gafsa, phosphates de Maroc 32% et 34%, pulvérisés aux tamis 100 et 300, ont été préparés en usine au départ d'un lot de 5 tonnes chacun du phosphate brut respectif (J, K et L).

Chacun des échantillons ci-dessus a été soumis aux essais suivants :

- (1) analyse chimique élémentaire
- (2) solubilité dans divers réactifs neutres ou acides
- (3) microphotographies optiques
- (4) analyse granulométrique.

5° - surface spécifique externe,

6° - surface spécifique totale,

7° - densité réelle à l'hélium,

8° - densité apparente.

*Analyse chimique élémentaire —*

L'analyse de chaque échantillon a été effectuée sur le produit séché à 100°. Les résultats sont réunis dans le tableau n° 1.

*Analyse de la solubilité —*

Le tableau n° 2 donne en pour cent de l'échantillon et en pour cent du  $P_2O_5$  total, les résultats de ces analyses.

On remarque dans ce tableau que, en ce qui concerne les phosphates nord africains, la solubilité d'un même phosphate augmente avec la finesse de pulvérisation de celui-ci.

(Voir tableaux n° 1 et n° 2).

*Microphotographies optiques —*

Les planches microphotographiques ci-jointes donnent les résultats des examens au microscope ordinaire.

Tous les échantillons ont été soumis, d'une part, à l'examen microscopique en lumière incidente sur fond noir, à sec, sans dispersion, afin d'étudier l'état d'agglomération. Grossissement : 120.

Dans ces conditions, les échantillons de phosphates bruts se présentent sous forme de gros blocs dont la plupart sont des agglomérats (ordre de grandeur 0,25 mm). Les échantillons pulvérisés forment des masses compactes à peu près identiques.

On a procédé, d'autre part, à l'examen microscopique en lumière transmise, après dispersion dans l'huile de paraffine. Grossissement : 70. Les différents échantillons présentent en moyenne les dimensions suivantes :

A — 30 à 100  $\mu$

B — 10 à 50 „

C — 15 à 90 „

D — 15 à 70 „

E — 15 à 90 „

F — 15 à 70 „

G — 15 à 90 „

H — 15 à 70 „

I — 25 à 70 „

TABLEAU n° 1

[illegible]

TABLEAU n° 2

	J—Gafsa 30% brut		A—Gafsa 30% tamis 100		B—Gafsa 30% tamis 300		K—Maroc 32% brut		C—Maroc 32% tamis 100		D—Maroc 32% tamis 300	
	% de phosph.	% de $P_2O_5$ total	% de phosph.	% de $P_2O_5$ total	% de phosph.	% de $P_2O_5$ total	% de phosph.	% de $P_2O_5$ total	% de phosph.	% de $P_2O_5$ total	% de phosph.	% de $P_2O_5$ total
Citrate neutre	—	1.78	5.9	3.60	11.9	4.59	15.1	2.17	6.6	3.19	9.9	3.57
Acide citriques 2%—	meth. Wagner	10.5	34.8	10.9	36.0	12.3	40.7	6.3	19.3	8.5	26.3	9.8
„	— meth. Robertson	25.2	83.3	25.1	83.0	29.2	96.6	17.9	55.0	29.5	82.0	30.4
Acide lactique 2%—	meth. Wagner	13.8	45.8	11.4	37.72	14.3	47.4	9.6	29.5	12.1	37.5	12.2
„	— meth. Robertson	24.7	81.8	27.6	91.2	28.9	96.0	24.2	74.5	27.2	84.2	30.1
Acide formique 2%—	meth. Wagner	16.2	53.7	18.1	59.8	21.9	72.7	16.1	49.6	18.3	56.7	20.1
„	— meth. Robertson	28.2	93.4	28.7	94.9	29.6	97.9	28.8	88.7	30.8	95.5	31.7

	L—Maroc 34% brut		E—Maroc 34% tamis 100		F—Maroc 34% tamis 300		G—Constantine Agrophos		H—Floride tamis 300		I—Kola tamis 300	
	% de phosph.	% de $P_2O_5$ total	% de phosph.	% de $P_2O_5$ total	% de phosph.	% de $P_2O_5$ total	% de phosph.	% de $P_2O_5$ total	% de phosph.	% de $P_2O_5$ total	% de phosph.	% de $P_2O_5$ total
Citrate neutre	—	1.82	5.3	3.47	10.1	3.67	10.7	1.98	7.7	3.12	9.3	2.14
Acide citrique 2%—	meth. Wegner	6.6	19.4	9.8	28.9	10.5	30.9	8.5	32.9	7.3	21.7	3.3
„	— meth. Robertson	19.5	57.0	25.0	73.4	30.6	90.0	21.8	84.8	21.4	64.1	7.5
Acide lactique 2%—	meth. Wagner	8.6	25.2	11.7	34.4	12.8	37.7	7.6	29.4	5.9	17.8	3.1
„	— meth. Robertson	18.9	55.3	28.4	83.6	30.4	89.3	23.3	90.5	16.9	50.8	7.7
Acide formique 2%—	meth. Wegner	14.8	43.1	17.5	51.3	18.9	55.7	14.9	58.1	7.3	21.7	2.7
„	— meth. Robertson	26.1	76.2	31.8	93.3	32.8	96.4	24.8	96.6	24.7	74.1	8.7

Les échantillons passés au tamis 100 ont encore une répartition de grosseur des particules très variée. Ceux passés au tamis 300 sont un peu plus homogènes. Ils se distinguent peu les uns des autres au point de vue forme et aspect des particules, sauf l'échantillon I (phosphate de Kola) qui est nettement plus cristallisé.

#### Analyse granulométrique—

Méthode—Dispersion dans un mélange gomme-sucre, et analyse de la répartition des tailles de particules d'après leurs vitesses de sédimentation.

Les analyses granulométriques ont montré que les neuf échantillons examinés (A à I) se divisent en deux catégories :

- 1°—les tamis 100, dont fait partie l'échantillon G (Agrophos)
- 2°—les tamis 300.

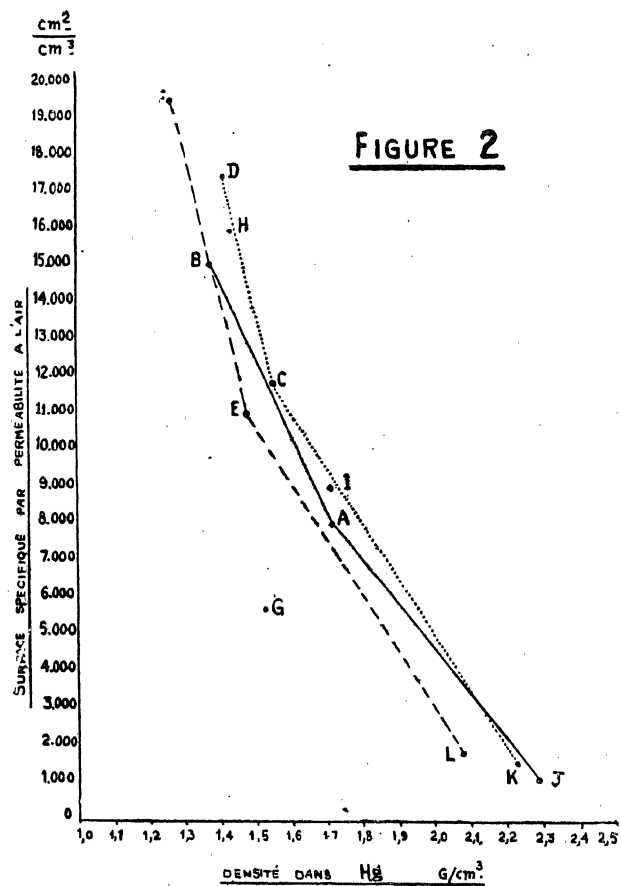
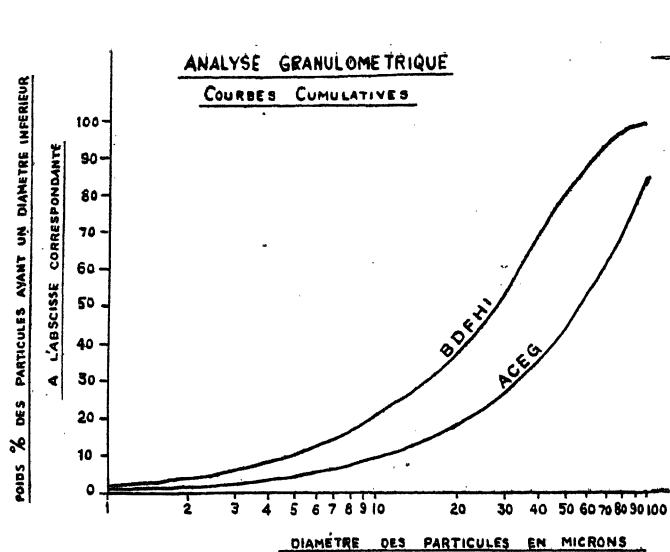
Dans chacune de ces catégories, les différences sont très faibles et de l'ordre de grandeur des erreurs d'expérience ou de prise d'échantillon. Comme il n'est pas possible d'assurer la réalité de ces différences, on donnera donc simplement la moyenne de granulométrie pour chacune des deux catégories. Il convient également de signaler la présence de 2 à 3% de parties solubles, dont il n'est pas tenu compte dans les résultats ciaprès :

TABLEAU n° 3

Dimensions des particules (diamètre) mu.	Poids des particules	
	Echantillons A C E G tamis 100	Echantillons B D F H I tamis 300
100	15	1
de 100 à 50	40	19
50 à 30	18	25
30 à 10	18	35
10 à 3	6	14
3 à 1	2	4
1	1	2

La figure 1 représente les courbes cumulatives de répartition des tailles, tracées d'après ces valeurs ; en ordonnées le poids % des particules ayant un diamètre inférieur à l'abscisse correspondante ; en abscisses (échelle logarithmique) le diamètre des particules, en microns.

Ces courbes confirment, d'une part, la variété des tailles présentes dans chaque échantillon malgré le tamisage et, d'autre part cependant, la différenciation apportée par la finesse des deux tamis. La valeur supérieure des tailles, observée grossièrement au microscope ordinaire, est du bon ordre de grandeur, comparée aux résultats de l'analyse granulométrique, et sépare assez bien les tamis 100 et 300.



## Mesures de surface et de densité—

### Méthodes—

#### Surface spécifique totale :

Mesure de l'adsorption d'azote à  $-195^{\circ}\text{C}$ . sur l'échantillon dégagé sous vide. Interprétation de la branche initiale de l'isotherme selon la théorie de BRUNAUER, EMMET et TELLER.

#### Surface spécifique externe :

Mesure par perméabilité à l'air d'une couche de la substance étudiée; la résistance offerte par cette couche au flux d'air qui la traverse est en relation avec la surface externe des particules qui composent la couche.

#### Densités réelles à l'hélium :

Mesure du volume occupé par la substance (dans un récipient de volume connu) grâce à la pesée de la quantité de mercure nécessaire pour comprimer l'hélium jusqu'à la pression qu'avait ce gaz avant détente dans le récipient évacué.

#### Densités apparentes dans le mercure :

Pesée de la quantité de mercure nécessaire pour remplir un picnomètre contenant la substance, l'entrée du mercure se faisant sous vide et la mesure étant effectuée après établissement d'une pression de 1 atm. sur le mercure.

Le tableau n° 4 ci-après rassemble les résultats numériques des mesures de surface et de densité.

TABLEAU n°. 4

Echantillon référéncié		Surface totale m <sup>2</sup> /gr	Surface extérieure cm <sup>2</sup> /cm <sup>3</sup>	Densité dans He g/cm <sup>3</sup>	Densité dans Hg g/cm <sup>3</sup>
J—Gafsa brut	...	21.9	1.300	2.83	2.29
A— „ t. 100	...	22.0	8.000	2.96	1.72
B— „ t. 300	...	21.8	15.200	2.93	1.38
K—Maroc 32 brut	...	16.0	1.600	2.98	2.23
C— „ t. 100	...	16.8	11.800	2.92	1.54
D— „ t. 300	...	15.5	17.500	3.00	1.41
L— „ 34 brut	...	19.6	1.900	3.09	2.07
E— „ t. 100	...	20.5	11.000	3.05	1.49
F— „ t. 300	...	20.5	19.600	3.02	1.27
G—Agrophos	...	20.3	5.700	2.88	1.53
H—Floride t. 300	...	11.9	16.000	2.96	1.43
I—Kola t. 300	...	1.2	9.000	3.20	1.72

Les mesures de surface totale (par adsorption d'azote) font ressortir que les échantillons d'un même phosphate ont une même surface quelle que soit la finesse du tamisage :

J A B (Gafsa 30%) = 22 m<sup>2</sup>/gr

K D C (Maroc 32%) = 16 m<sup>2</sup>/gr

L E F (Maroc 34%) = 20 m<sup>2</sup>/gr environ.

L'échantillon G (Agrophos) a une surface spécifique totale analogue à celle du phosphate L E F L'échantillon H a une surface plus petite (12 m<sup>2</sup>/gr). Quant à l'échantillon I (Kola), sa surface totale est très faible (1,2 m<sup>2</sup>/gr).

On peut en conclure que tous les échantillons, à l'exception du phosphate I, sont probablement poreux puisque, d'une part, leur surface totale ne varie pas avec le tamisage et que, d'autre part, cette surface totale est beaucoup plus grande que la surface externe (de 10 à 20 fois).

Des mesures d'adsorption d'azote poussées jusqu'aux fortes pressions relatives permettraient de confirmer cette conclusion en déterminant la porosité totale et la répartition du volume poreux en fonction de la taille des pores dans chacun de ces échantillons.

Au contraire, l'échantillon I semble non poreux. En effet, d'une part sa surface totale est très faible (1,2 m<sup>2</sup>/gr) et du même ordre de grandeur que sa surface externe (0,5 à 1,0 m<sup>2</sup>/gr) (voir tableau n° 6) d'après la perméabilité à l'air, la densité apparente et la granulométrie. D'autre part, sa densité réelle est forte (3,2 au lieu de 3,0 pour les autres phosphates). Enfin son aspect au microscope est nettement cristallisé, à la différence des autres échantillons.

Les résultats des mesures de perméabilité à l'air et de densité dans le mercure doivent présenter entre eux une certaine corrélation, car ces techniques caractérisent toutes deux des propriétés d'encombrement externe;

Sur la figure 2, on a représenté, pour les 12 échantillons, les valeurs de la surface extérieure en fonction de la densité apparente. On voit tout d'abord que, mis à part l'échantillon G (Agrophos), tous les points représentatifs se placent entre deux lignes limites très resserrées ; il n'aurait pas été impossible de tracer une courbe moyenne unique.

*Pour un même phosphate (ex. J-A-B ou K-C-D ou L-E-F) les surfaces extérieures augmentent, ainsi qu'il est normal, avec la finesse de tamisage.*

Pour un même phosphate les densités apparentes dans le mercure diminuent, au contraire, quand on passe du phosphate brut au phosphate tamis 100, puis au phosphate tamis 300.

Cela provient de ce que la mesure picnométrique au mercure dépend de la taille des vides laissés entre les particules d'échantillon ; sous la pression finale de 1 atm. utilisée, le mercure ne peut pénétrer dans les vides trop petits ; comme ces vides sont individuellement des tailles de l'ordre de grandeur des particules qui les entourent, le mercure occupe plus de place dans le picnomètre rempli de gros grains que dans le picnomètre contenant de petits grains ; il en résulte une densité apparente du phosphate d'autant plus faible que la poudre échantillon est plus fine.

On observe sur la figure 2 que les échantillons bruts (J-K-L) se groupent entre eux de même que les échantillons tamis 100 (A-C-E) et les échantillons tamis 300



(B D F). L'échantillon H (Floride tamis 300) se classe bien avec ceux de la catégorie, mais l'échantillon I (Kola tamis 300) se classe avec le tamis 100 et l'échantillon G (Agrophos) se place tout-à-fait en dehors de la courbe.

Les mesures de densité réelle dans l'hélium appellent les observations suivantes : la précision des mesures n'est pas suffisante pour attribuer une signification réelle au chiffre des centièmes. Telles quelles, les valeurs obtenues permettent de conclure que tous les échantillons ont à peu près la même densité réelle (environ 3,0) sauf l'échantillon I (Kola tamis 300) qui a une densité plus forte (3,20). Les échantillons J et G ont d'autre part une densité sensiblement plus faible (2,8 et 2,9) mais les mesures sur J sont sujettes à caution car l'échantillon contient beaucoup de cailloux qui rendent très hétérogènes les prises d'essai.

Si l'on veut cependant accorder une confiance plus grande aux résultats numériques figurant dans le tableau (résultats dont chacun est la moyenne de nombreux essais), on peut reconnaître certaines différences secondaires dans la densité réelle des divers phosphates. En considérant en effet que le même phosphate garde la même densité réelle, quel que soit son tamisage, et en tenant compte des réserves formulées concernant l'hétérogénéité de l'échantillon J, on peut grouper les résultats comme suit, par ordre de densité réelle croissante (tableau 5) :

TABLEAU n° 5

Agrophos	(?) 2.83 (J)	2.88 (G)		2.88
Gafsa 30 %		2.96 (A)	2.93 (B)	2.91 (?)
Floride	2.98 (K)		2.96 (H)	2.96
Maroc 32%	3.09 (L)	2.92 (C)	3.00 (D)	2.97
Maroc 34%		3.05 (E)	3.02 (F)	3.05
Kola			3.20 (I)	3.20

A partir des valeurs figurant au tableau de l'analyse granulométrique, on peut calculer une valeur *approchée* de la surface externe des échantillons :

$$S = \frac{6}{100\rho} \sum_i \frac{y_i}{d_i}$$

où S est la surface externe (en M2/gr,  $\rho$  la densité des particules (en gr/cm3) et  $y_i$  le % en poids des particules ayant un diamètre  $d_i$  (microns).

Appliquée aux deux séries d'échantillons (tamis 100 et 300), cette formule donne les résultats suivants en prenant pour densité une valeur moyenne de 3,0 (donnée par les mesures de densité dans l'hélium) et en prenant pour taille moyenne dans chaque intervalle granulométrique, la taille inférieure de l'intervalle :

Echantillons A C E G :

$$S_1 = \frac{6}{300} \left( \frac{1}{0,1} + \frac{2}{1} + \frac{6}{3} + \frac{18}{10} + \frac{18}{30} + \frac{40}{50} + \frac{15}{100} \right)$$

soit  $S_1 = 0,5$  m2/gr environ.

Echantillons B D F H I :

$$S_2 = \frac{6}{300} \left( \frac{2}{0,1} + \frac{4}{1} + \frac{14}{3} + \frac{35}{10} + \frac{25}{30} + \frac{19}{50} + \frac{1}{100} \right)$$

soit  $S_2 = 1 \text{ m2/gr}$  environ.

Une autre manière d'obtenir la surface extérieure par gramme consiste à utiliser les données de la perméabilité à l'air et de la densité dans le mercure.

$$S \text{ m2/gr} = \frac{S \text{ perm. (cm2/cm3)}}{10 \cdot 000 \times d_{Hg} \text{ (gr/cm3)}}$$

On obtient ainsi les valeurs suivantes, que l'on peut comparer à celles déduites de la granulométrie (tableau n°6) :

TABLEAU n° 6

Echantillon	$\frac{S \text{ perm}}{10 \cdot 000 \times d_{Hg}}$	$\frac{6}{100 d \text{ (He)}} \text{ i } \frac{y_1}{d_1}$
A	0.5 m2/gr.	0.5 m2/gr
B	1.1 „	1.0 „
C	0.8 „	0.5 „
D	1.2 „	1.0 „
E	0.7 „	0.5 „
F	1.5 „	1.0 „
G	0.4 „	0.5 „
H	1.1 „	1.0 „
I	0.5 „	1.0 „

Les approximations incluses dans les hypothèses qui sont à la base de ces calculs interdisent d'espérer des concordances quantitatives, mais les ordres de grandeur sont retrouvés ; la plus forte divergence s'observe pour l'échantillon I (phosphate Kola, tamis 300).

#### Conclusion :

Ces premiers résultats font apparaître :

- 1°—que, parmi les phosphates naturels de chaux étudiés, le phosphate de Gafsa 30. présente la plus grande surface spécifique totale.
- 2°—que la solubilité des phosphates naturels est liée, outre, comme on sait, à la finesse des particules ainsi qu'à des facteurs de composition, à la surface spécifique totale. Celle-ci est donc un facteur important de la solubilité.
- 3°—le fait que la surface spécifique totale ne varie pas, ou varie très peu, pour un même phosphate, avec la finesse de mouture de celui-ci, semble démontrer que les proes des agrégats ou des particules s'ouvrent à l'extérieur.

L'exécution pratique de ce travail a été confiée au Laboratoire Central des Services Chimiques de l'Etat à Paris.

### SUMMARY

The Authors are reporting the results obtained on measurings of texture, which they have carried out on a series of sedimentary rock phosphates and which can be interpreted in terms of availability to plants of the phosphates present in form of fertilizers.

They lay an emphasis on the following :

1. The total specific surfaces, with a constant granule size, vary according to the type of phosphate: between the phosphates which have been investigated the largest total specific surface belongs to the Gafsa phosphate.
2. The solubility in the conventional reagents, and the availability of rock phosphates are connected with the total specific surface.
3. The total specific surface of a given phosphate does not vary much according to the general granule size of the type of phosphate. This statement tends to justify the assumption of a fine spongoid structure of sub-miscroscopic range, with small channels being open towards the outside.

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